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LXIX. *The Emission of Electrons by X-Rays.* By  
G. SHEARER, M.A., 1851 Exhibition Scholar, Emmanuel  
College, Cambridge\*.

THE general object of this investigation was to obtain more definite information as to the emission of electrons from matter under the influence of X-ray bombardment.

(1) *Historical.*—Very shortly after the discovery of X-rays it was shown that all forms of matter emitted electrons when bombarded by X-rays. Later work revealed the fact that, in this emission, the electrons had all velocities up to a certain maximum; this maximum velocity can be determined by the quantum equations—

$$\frac{1}{2}mv^2 = Ve = h\nu,$$

where  $e$ ,  $m$ ,  $v$  represent the charge, mass, and maximum velocity of the electrons,  $\nu$  the frequency of the X-rays,  $V$  the applied potential, and  $h$  Planck's constant.

In addition to this general electron emission, there is a special emission associated with the characteristic X-radiation of the matter bombarded. Until recently there has been some doubt as to the exact nature of this special emission. Experiments by Barkla and the author † failed to reveal any special distribution of velocity associated with these electrons.

\* Communicated by Prof. Sir E. Rutherford, F.R.S.

† Barkla and Shearer, *Phil. Mag.* xxx. p. 746 (1915).

On the other hand, Robinson and Rawlinson\* by the magnetic spectrum method showed that there were present groups of electrons with special velocities. Kang Fuh Hu† also obtained some evidence of the existence of these groups. Simons‡ carried out experiments on the same lines as those of Barkla and Shearer, and concluded that sub-groups of electrons were present when the characteristic X-radiations of the bombarded matter were excited. Recently the question has been definitely settled by the experiments of De Broglie§. By the use of the magnetic spectrum method he has shown that the energies of these groups correspond to  $h(\nu - \nu_K)$ ,  $h(\nu - \nu_L)$ , &c., where  $\nu$ ,  $\nu_K$ ,  $\nu_L$ , &c., represent the frequencies of the incident radiation and of the K, L, &c. radiations of the matter bombarded. Similar results have recently been obtained by Whiddington||.

While these experiments show that the electronic radiation consists of a general emission corresponding to the "white" radiation from the tube and groups of electrons whose energies obey simple quantum relations, they tell us nothing of the magnitude of the emission, nor of how this magnitude depends on the type of matter from which the electrons are ejected.

Laub¶ showed that the efficiency of an element as a source of electrons increased with its atomic weight, but made no attempt to obtain a law governing the variation. Moore\*\*, as a result of some experiments on the relative ionizations produced in various gases, deduced the law that the number of electrons emitted per atom is proportional to the fourth power of the atomic number. These experiments were of a somewhat indirect nature, and the range of atomic number investigated was small.

The experiments described here were undertaken, primarily, to throw light, if possible, on this question.

(2) *Experimental Arrangements*.—In order to avoid the difficulties of interpretation introduced by the use of ionization methods, it was decided to measure directly the number of electrons emitted by observing the rate at which an insulated radiator acquired a positive charge under the influence of X-ray bombardment.

\* Robinson and Rawlinson, *Phil. Mag.* xxviii. p. 277 (1914).

† Kang Fuh Hu, *Phys. Rev.* xi. p. 505 (1918).

‡ Simons, *Phil. Mag.* xli. p. 120 (1921).

§ De Broglie, *Journ. de Phys.* (6) ii. p. 265 (1921).

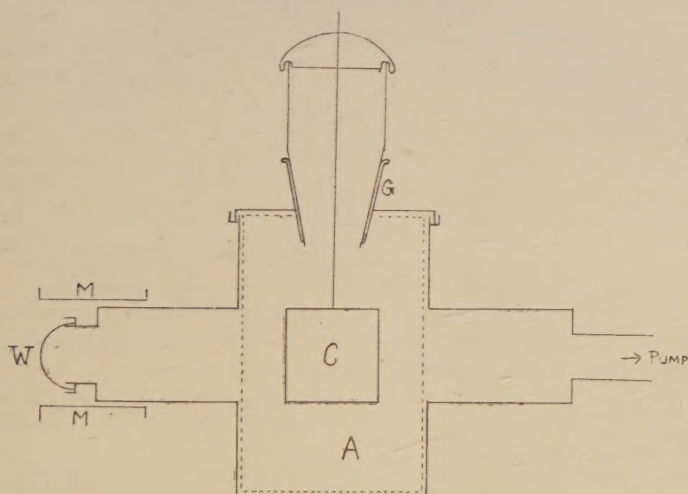
|| Whiddington, *Phil. Mag.* June 1922.

¶ Laub, *Ann. der Phys.* (4) xxviii. p. 782 (1908).

\*\* Moore, *Proc. Roy. Soc. A.* xix. p. 337 (1915).

Fig. 1 shows the final form of the apparatus used. Rays from an X-ray tube enclosed in a thick lead box passed through a small aperture in the box and entered the cylindrical brass examination vessel A through a hemispherical glass window W. Inside the vessel, in the path of the rays, was suspended an insulated brass cube C, which served to carry the materials to be examined. In order that more than one substance might be investigated without dismantling the apparatus, the cube was made capable of rotation about a vertical axis by means of a ground-glass joint G, which carried the whole of the insulated system.

Fig. 1.



By turning this joint through  $90^\circ$  at a time different materials could be exposed to the action of the rays. The beam of X-rays was such that the cross-section was never as large as the area of the material under examination, so that only the window and the matter on the face of the cube were exposed to direct X-ray bombardment. An electromagnet M was arranged near the window so that any electrons from the window might be bent back into the walls of the vessel and thus prevented from reaching the cube. The inside of the vessel was lined with filter paper to reduce the effect of the scattered and characteristic radiations from the cube. Inside the vessel and insulated from it was placed a wide-meshed wire cylinder which could be charged to any desired potential.



The vessel was connected by wide-bore glass tubing to a Gaede mercury pump. A charcoal-filled tube was attached and cooled with liquid air. By these means the vessel was kept at a very low pressure so as to make all ionization effects negligible. As an additional precaution, hydrogen was used as residual gas in some of the experiments.

The substances to be examined were mounted on the faces of the cube, and were all of sufficient thickness to give the maximum electron emission.

The source of X-rays was a Coolidge tube with a tungsten anticathode. This was actuated by a Butt induction coil and mercury interrupter. Owing to the smallness of the effect to be measured, it was not possible to use a monochromatic source of X-rays.

The rod carrying the cube was connected through earthed shielding tubes to a string electrometer. The rate at which this acquired a positive charge was taken as a measure of the electron emission, and was determined for various substances. In order to correct for small variations in the intensity of the rays during a set of observations, a standardizing ionization chamber was fitted. This was connected to a Dolezalek electrometer of low sensitivity, a steady deflexion method being used.

(3) *General Results.*—The early results with this apparatus showed that the electron emission was of a more complicated nature than had been anticipated.

If the cube was allowed to charge up to a considerable potential, it was found that the rate of charging up fell off rapidly at first and only became steady after a potential of from ten to twenty volts had been reached. Such an effect might have been due to ionization effects, but a simple calculation showed that the magnitude of the effect was very much larger than that due to the ionization of a gas at a pressure of  $\cdot 01$  mm., and the pressure in the vessel was certainly less than  $\cdot 001$  mm. It appeared, therefore, that this effect was due to the presence of a large number of slow electrons. When the cube attained a voltage of from ten to twenty volts the electric field was of sufficient strength to prevent the escape of such electrons.

The existence of these low-speed electrons was also suggested by certain observations on the effect of the magnetic field used to deflect the electrons from the window. It was found that this field reduced the emission from the cube although the stray field at the surface of the cube was not more than a few Gauss.



In these experiments the surface of the cube was perpendicular to the direction of propagation of the X-rays, and therefore parallel to the direction of the electric vector in the X-ray beam. It was possible, therefore, that there was a large number of electrons whose initial direction was nearly parallel to the surface of the cube. Such electrons, even if their velocities were considerable, might be bent back into the cube by electric or magnetic fields of relatively small strength. This hypothesis was tested by comparing the reducing effect of electric and magnetic fields when the angle of incidence was  $90^\circ$  and  $45^\circ$ . It was found that the percentage reduction was the same in the two cases. Had the effect been due to the bending back of electrons emitted in directions approximately parallel to the face of the cube, the reduction of the emission would have been larger in the first case than in the second.

The conclusion reached was that, in addition to the high-speed electron emission, there exists also an emission of electrons of low speed. After considerations such as these had led the writer to this conclusion, it was found that similar effects had previously been observed by Campbell \* in his work on delta rays.

In what follows, first the properties of the high-speed electrons and then those of the slow electrons will be discussed.

#### A. High-Speed Emission.

(4) *Relative Electron Emission from Metals.*—The effect of the low-speed electrons was eliminated by charging the inner wire cylinder to a voltage sufficient to prevent their escape from the surface of the cube. The residual effect was then that due to the high-speed electrons.

The metals investigated were Aluminium, Iron, Nickel, Copper, Silver, Tin, Gold, Lead, and Bismuth. The X-ray tube was operated under varying conditions, and it was found that the relative values for the various metals depended very little on the conditions of the tube. This point will be discussed more fully later.

Table I. shows the results obtained, the value for the tin being taken as 100.

TABLE I.

Radiator .....	Al.	Fe.	Ni.	Cu.	Ag.	Sn.	Au.	Pb.	Bi.
Electron Emission .....	11	47	53	56	94	100	184	189	194
Atomic Number .....	13	26	28	29	47	50	79	82	83
Atomic Weight .....	27	56	59	67	108	119	197	207	208

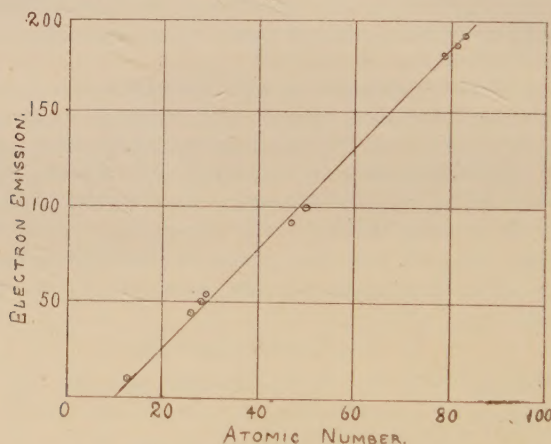
\* N. R. Campbell, Phil. Mag. xxiv. p. 783 (1912).

It is clear that the efficiency of a metal as a source of electrons increases with its atomic weight or number. Fig. 2 shows the results graphically. The relation between the number of electrons escaping from a metal and its atomic number is very nearly a linear one. The electron emission may be expressed with considerable accuracy by an equation of the form

$$n' = k(N - a),$$

where  $n'$  is the number of electrons escaping from the metal,  $N$  is the atomic number, and  $k$  and  $a$  are constants, the value of  $a$  being approximately 10.

Fig. 2.



Since  $N$  denotes the number of electrons in the atom, it might appear that this result implies that the number of electrons emitted from an atom is proportional to the number of electrons in the atom with a small correction due to the presence of the term  $a$  in the equation. Such an interpretation is, however, not permissible, as what has been measured in these experiments is the number of electrons which succeed in escaping, and not the number liberated from the atoms under bombardment.

In the present state of knowledge of the laws governing the passage of electrons through matter, it is not possible accurately to deduce the number of electrons liberated from an atom from the observed number actually escaping from the surface. An approximation may, however, be obtained by making certain assumptions which are probably near the truth.

In the first place, let it be assumed that the number of electrons escaping from the radiator falls off exponentially with the depth from which they come. If  $I_0$  is the initial intensity of the X-rays,  $S$  the area bombarded,  $n$  the number of electrons liberated per unit volume per unit time per unit intensity, and  $\mu_1$  and  $\mu_2$  the absorption coefficients of the X-rays and electrons in the radiator, then the number of electrons from a layer  $dx$  at a depth  $x$  which actually escapes is

$$dn' = n \cdot S \cdot I_0 e^{-(\mu_1 + \mu_2)x} dx.$$

The total number escaping is therefore

$$n' = nSI_0/(\mu_1 + \mu_2).$$

Hence, since  $\mu_1$  is small compared with  $\mu_2$ ,

$$n' = \frac{NSI_0}{\mu_2}.$$

If, on the other hand, it is assumed that the number escaping falls off exponentially with the distance traversed by the electrons in the radiator, the following expression is obtained :

$$n' = nSI_0/4\mu_2^*$$

where  $\mu_2$  is the exponential coefficient of absorption for the electrons.

Whichever of these two absorption laws is taken, it follows that the number of electrons liberated per unit volume is proportional to  $\mu_2$  times the number actually escaping. From this the number liberated per atom can easily be derived.

If  $A$  is the atomic weight of the radiator,  $m$  the mass of the hydrogen atom, and  $\rho$  the density, the number of atoms

\* The actual expression for  $n'$  is

$$n' = \frac{1}{2}nSI_0 \int_0^\infty \left[ e^{-(\mu_1 + \mu_2)x} - \mu_2 x e^{-\mu_1 x} \int_x^\infty \frac{e^{-\mu_2 r}}{r} dr \right] dx,$$

which, on evaluation, gives

$$n' = \frac{1}{2}nSI_0 \left[ \frac{1}{\mu_1} - \frac{\mu_2}{\mu_1^2} \log \left( 1 + \frac{\mu_1}{\mu_2} \right) \right].$$

If this is expanded in terms of  $\frac{\mu_1}{\mu_2}$ , and  $\frac{\mu_1^3}{\mu_2^3}$  is neglected, it gives the result quoted above.



per unit volume is  $\rho/Am$ . Hence the number of electrons liberated per atom per unit time per unit intensity is

$$\frac{nAm}{\rho},$$

or, substituting for  $n$  in terms of  $n'$ ,

$$k \cdot Amn' \cdot \frac{\mu_2}{\rho},$$

where  $k$  is a constant depending on the exact form of the absorption law chosen.

- If it is assumed that Lenard's law that  $\frac{\mu_2}{\rho}$  is constant holds under the conditions obtaining in these experiments, the result of these calculations is that the number of the electrons liberated per atom per unit time per unit intensity is proportional to the product of the number of electrons actually escaping and the atomic weight of the substance from which they are liberated.

It has been shown that the experimental results led to the conclusion that  $n'$  was proportional to  $(N-10)$ . Hence the number of electrons liberated per atom is proportional to

$$A \cdot (N-10).$$

In deducing this result several assumptions have been made, some of which are only rough approximations to the truth. Probably the most serious one is that Lenard's law—that  $\mu_2/\rho$  is constant—can be applied to this case. Even under the conditions of Lenard's experiments, the result was only an approximate one. A strong argument in favour of its application to these experiments is that it causes the density to disappear from the final correction to be applied to the observed electron emissions. The values for the electron emissions from the elements gold, lead, and bismuth were found to be approximately equal. On the other hand, the densities of these elements are 19.32, 11.37, and 9.80 respectively. If the correction to be applied to deduce the electron emission per atom were a function of the density, all regularity would disappear from the results. If the correction depends only on the atomic weight or atomic number, no such difficulty presents itself.

When this result is compared with the only other result so far obtained, a serious disagreement presents itself. Moore\* found that the electron emission per atom was proportional

\* *Loc. cit.*

to the fourth power of the atomic number. This result was obtained indirectly from observations on the relative ionizations of different gases. The heaviest element used was chlorine, so that the range of Moore's experiments falls almost entirely outside that of these experiments. Had it not been for the fact that Moore's law fits in well with the absorption law of Bragg and Peirce, we might have concluded that both his law and that deduced here are both approximations to a more general law, the former being an approximation holding for elements of low atomic weight, while the latter is a better approximation for the heavier elements. Bragg and Peirce\* have shown that the X-ray energy absorbed per atom is proportional to the fourth power of the atomic number of the absorbing element. The combination of this result with that of Moore suggests that the number of electrons emitted is proportional to the X-ray energy absorbed, a result pointed out by Moore. The range of elements used in the experiments of Bragg and Peirce was well within that of these experiments although outside that of Moore's. On the other hand, if the above results are true, no such simple law appears to hold. Even when allowance is made for the approximate nature of the various assumptions made in deducing the final result, it is extremely difficult to see any way in which these experiments could possibly be reconciled with a fourth-power law.

In connexion with this result, it is of interest to refer to a result obtained by Kaye† on the relative efficiency of various metals as anticathodes in an X-ray tube. Kaye found that the X-ray output of a tube increased linearly with the atomic weight of the metal used as anticathode in the tube. Later experiments by Duane and Shimizu‡ showed that the proportionality was to the atomic number rather than the atomic weight. In these experiments we are dealing with the transformation of electron energy into X-ray energy, while the problem that is the subject of this paper is the inverse one—that of the transformation of X-ray energy into electronic energy. It has been shown that there is a linear relation connecting the number of electrons escaping from a metal bombarded by X-rays and the atomic number of the metal. These results imply that, when the number of electrons entering a metal is kept constant—as in Kaye's experiments,—the X-ray energy emitted is a linear function

\* Bragg and Peirce, *Phil. Mag.* xxviii. p. 626 (1914).

† Kaye, *Phil. Trans. A.* 209, p. 123 (1908).

‡ Duane & Shimizu, *Phys. Rev.* xiv. p. 525 (1919).



of the atomic number, while, if the X-ray energy falling on a metal is kept constant, the number of electrons emerging from the metal is again a linear function of the atomic number of the metal.

(5) *Experiments with Substances other than Metals.*—Certain experiments were carried out on the electron emission from salts. Only a few salts were tried, and the data are not sufficiently extensive to warrant the deduction of definite conclusions. The chief salts investigated were  $\text{As}_2\text{O}_3$ , KI, and RbI. These were chosen in the hope that they would throw light on the electron emission from the elements Arsenic, Rubidium, and Iodine, and thus serve to fill up some of the gaps in the electron emission-atomic number curve obtained from the investigation of the metals. The values found for these salts, with tin taken as 100, were 47, 128, and 158 respectively. The values for KI and RbI were both much higher than is to be expected if the effect is an additive one and the values of the electron emission were such as would result from the interpolation from fig. 2. The atomic numbers of K, Rb, and I are 19, 37, and 53, so that, if the effects are additive, it is to be expected that the values for these iodides would be less than 100, whereas it was found that they were considerably in excess of this value. These salts were placed on the faces of the cube in the form of a layer of small crystals, and it is possible that the effective area under bombardment was thus considerably greater than in the case of a sheet of metal. In spite of this possibility, it seems difficult to account for the high values obtained for these salts. It is interesting to note that the elements potassium and rubidium are both very active from a photoelectric and thermionic point of view.

A few experiments were made on other salts of potassium. It was shown that the electron emission increased with the molecular weight of the salt. Thus, both the carbonate and the sulphate gave very much smaller value than the iodide, while the effect from the sulphate was greater than that from the carbonate.

(6) *Special Electron Emission.*—It has long been known that when a characteristic radiation of an element is excited there is an increase in the electron emission.

Although, in these experiments, no attempt was made to use monochromatic radiations, still it was expected that it would be easy to detect this special electron emission. In order to test for its effect, observations on two metals—especially copper and tin—were made under widely varying



conditions of the X-ray tube. The voltage of the tube was varied and the ratio of the electron emissions from the two metals was measured. Results of such measurements are given in Table II. The observations have been taken in groups, each group corresponding to a certain range of potential on the tube, the potential being measured by the equivalent spark-gap between points.

TABLE II.

Range of Spark-Gap.	Cu/Sn.
0- 5 cm.	0.57
5- 9 „	0.55
9-12 „	0.55
12->12 „	0.56

It is clear from this table that, under the experimental conditions, the ratio of the electron emission from these elements is practically independent of the potential used to excite the tube. It was expected that there would be a discontinuity in the ratio at the point where the K-radiations of tin became prominent. This should occur at a potential of about 50,000 volts. No such discontinuity appeared.

The reason probably lies in the fact that in these experiments the tube was fitted with a tungsten anticathode. The applied potential was never sufficient to excite the K-radiations of tungsten to any extent, while the L-radiations would be very largely absorbed in the walls of the tube and in the window of the examination vessel. Under these conditions, the radiation used was what is generally termed "white." Its quality varies with the potential used to excite the tube, but not to a very marked extent. Ulrey\* has shown that, under conditions which are very similar to those obtaining in these experiments, there is a maximum X-radiation at a wave-length which obeys the approximate law—

$$\lambda_{(\max.)} V^{\frac{1}{2}} = \text{constant},$$

where  $V$  is the applied potential. Thus quite a large difference in the potential produces a relatively small change in the position of the wave-length to which corresponds the maximum X-radiation.

It would appear, therefore, that the electron emission associated with the characteristic radiations of the elements bombarded is not of sufficient intensity as materially to affect

\* C. T. Ulrey, Phys. Rev. xi. p. 401 (1918).

these experiments; and these results are to be taken as representing what happens when the characteristic radiations are not excited to any extent.

In view of De Broglie's results, it is to be expected that many of the electrons emitted in connexion with the characteristic radiations will have relatively small velocities, and will, therefore, have difficulty in escaping from the radiator. Only a small fraction of those liberated will escape and contribute to the effect measured in these experiments.

(7) *Selective Emission in the Direction of Electric Vector.*—On the classical electromagnetic theory of light it seems probable that there will be a large preponderance of electrons emitted in the direction of the electric vector in the X-ray beam. In fact, the photographs obtained by C. T. R. Wilson seem to show that such is the case. In order to find evidence for such an effect, two adjacent sides of the cube were covered with the same metal, and measurements of the electron emission were made when the rays fell perpendicularly and at an angle of  $45^\circ$  on the metal. In the second case the area of metal under bombardment was 1.4 times the area in the first case, and for this reason an increase of 40 per cent. in the emission is to be expected. When the rays fall perpendicularly, electrons emitted in the direction of the electric vector should have difficulty in escaping from the metal, but when the angle of incidence is  $45^\circ$  this difficulty should not be so marked.

The results of such measurements made with lead as radiator showed an increase of 35 per cent. when the angle of incidence was  $45^\circ$ . This increase is rather more than accounted for by the increase of area of the radiator, and these observations show no evidence of any selective emission in the direction of the electric vector. It is probable that by the time that the electrons emerge from the metal their direction of motion is very different from what it was initially, owing to encounters with the atoms of the metal; and experiments such as these could not be expected to throw light on the initial direction of motion of the electrons. Wilson's photographs were taken with a gas as source of electrons, and in this case the initial direction of the electron is directly observed.

(8) *Variation of Electron Emission with Applied Voltage.*—A few experiments were carried out to see how the number of electrons emitted per unit intensity from any one radiator

varied with the voltage applied to the tube. Such experiments are rendered difficult by the necessity of obtaining some means of measuring the intensity of the X-ray beam. As a rough measure of this, the ionization produced in the standardizing vessel was used. The electron emission per unit intensity was measured for various potentials; Table III. gives a typical set of such observations.

TABLE III.

Voltage.	Electron Emission per Unit Intensity.	$nV^{\frac{1}{2}}$ .
28000	85	14200
36000	81	15400
45000	71	15000
65000	61	15500
78000	53	14800

This Table shows that the electron emission per unit intensity diminishes as the applied potential increases. Column 3 shows that the product of the number of electrons emitted per unit intensity and the square root of the voltage is approximately constant. Owing to the method adopted for the measurement of intensity, too much reliance must not be attached to this result, but it gives some indication of the nature of the variation.

This suggests an intimate connexion between this result and that obtained by Ulrey, to which reference has already been made. As an approximation the X-radiation used in these experiments may be considered as a monochromatic radiation of wave-length  $\lambda_{(\max.)}$ . Ulrey's result, combined with that just given, leads to the result that the number of electrons emitted per unit intensity is proportional to the wave-length, or inversely proportional to the frequency of the exciting radiation. As the size of the quantum is proportional to the frequency, this may be interpreted as meaning that the number of electrons emitted per unit intensity is directly proportional to the number of quanta involved.

### B. Low-Velocity Emission.

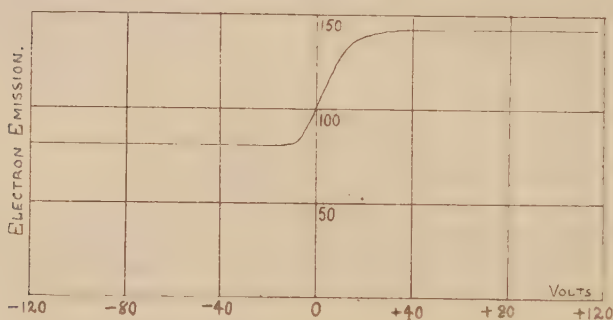
(9) In studying the properties of these electrons, the total number of electrons escaping from the radiator was measured under the influence of varying, accelerating, and retarding electric fields. For this purpose, the wide-meshed wire cylinder described above was charged to positive and



negative potentials, the walls of the vessel being connected to earth.

Under the influence of a retarding field the electron emission diminished rapidly at first, then more slowly, finally reaching a constant value. This stage was reached when a negative potential of about 20 volts had been applied. On the other hand, an accelerating field produced an increase in the emission, and the potential necessary to ensure constancy of the emission was considerably greater than in the case of a retarding field.

Fig. 3.



The curve in fig. 3 is typical of the effects of accelerating and retarding fields on the total electron emission. Such curves were obtained for various metals and for some salts. The results of these observations was that there did not appear to be any change in the velocity distribution of these slow electrons with a change in the nature of the matter from which they came. Exact quantitative measurements of the properties of these electrons were rendered difficult by the large effect which the state of the surface had on the emission. Especially in the case of the salts examined, fatigue effects were observed which were presumably of similar origin to those observed in the photo-electric effect. No special precautions were taken to obtain very clean surfaces. The state of the surface has very little effect on the emission of high-speed electrons, whose properties were the main object of this investigation.

Experiments made on the ratio of the number of low-speed electrons to the total emission showed that this was also independent of the material bombarded. Table IV. shows some of the results obtained in these measurements. The numbers have been reduced so that they all show the same electron emission with no field acting.

TABLE IV.

Voltage.	Cu.	Sn.	Pb.
0	100	100	100
+400	136	140	139
-400	81	79	80

The results of the following experiment throw some light on the source of these slow electrons. The wire cylinder was removed, and measurements were made on the effect of retarding fields. It was found that, under these conditions, the diminution was much more marked, and in some cases the brass cube even acquired a negative charge with a sufficiently large retarding field. This implied that more electrons were being driven from the walls into the cube than were coming from the cube owing to the direct action of the X-rays. As precautions had been taken to prevent the X-rays from falling directly on the walls of the vessel, the only sources of electrons from the walls were the high-speed electrons and the scattered and characteristic radiations from the cube. These X-radiations would be of small intensity compared with the direct X-ray beam, and their effect would be still further reduced by the paper lining. On the other hand, the walls were subject to direct bombardment by all the fast electrons, and it seems certain that it was this electronic bombardment which liberated the low-speed electrons. As the energy of the slow electrons is so small, it is reasonable to assume that one high-speed electron can produce a large number of low-speed electrons; and this would account for the observed fact that the number of electrons driven back by the action of the retarding field was greater than the number of electrons liberated by the X-ray beam. With the cylinder in position, the field between the walls and the cylinder prevented the electrons from the walls from reaching the central insulated system, while, owing to the wide mesh of the cylinder, the number liberated from it would be small.

The properties of these slow electrons are very similar to those of the delta rays produced by bombardment by alpha rays.

These results indicate that the low-speed emission is of a secondary nature, and owes its origin not to the direct action of the X-rays, but to the high-speed electrons ejected by the X-rays. The process appears to be exactly analogous to the phenomenon of ionization in a gas. The photographs obtained by C. T. R. Wilson show that each high-speed electron is

capable of ejecting a large number of slow electrons from the atoms with which it comes into collision. Exactly the same process should occur during the passage of electrons through a metal. In this case the number which will succeed in escaping will be relatively small owing to their low speed and consequent rapid absorption in the metal. The fact that quite a small accelerating field considerably increases the number of these electrons, shows that many of them are unable to escape unless their energy is increased by outside fields.

(10) *Summary of Results.*

(a) The electron emission from various metals and a few salts under the influence of X-rays has been measured, and an attempt has been made to deduce from these measurements the relation between the number of electrons emitted per atom per unit intensity per unit time and the atomic number or atomic weight of the substance from which they are liberated.

(b) It has been found that under these experimental conditions the special electron emission associated with the characteristic X-radiations of the substances bombarded is in these experiments only a very small fraction of the total electron emission.

(c) These experiments have yielded no evidence of any selective emission in the direction of the electric vector in the X-ray beam.

(d) It has been shown that the electron emission per unit intensity diminishes as the penetrating power of the radiation is increased.

(e) The properties of the low-speed electrons which accompany the high-speed emission have been investigated, and this emission has been ascribed to a secondary effect due to the action of the fast electrons.

This work was carried out at the Cavendish Laboratory, Cambridge, and the author has great pleasure in acknowledging the continual kindness and many helpful suggestions he has received during its progress from Prof. Sir Ernest Rutherford, F.R.S.



LXX. *Impact Ionization by Low-Speed Positive H-Ions in Hydrogen.* By A. J. SEXTON, M.Sc., Assistant Lecturer in Physics, The University of Sheffield\*.

*Introduction.*

THERE now exists a considerable amount of evidence on the conditions necessary to ionize a "normal" atom of a gas. In every case we are concerned with the energy exchanges between the atom to be ionized and the source of the ionizing energy.

We may formulate the conditions governing this interchange of energy as follows:—

(a) In order just to ionize a "normal" atom† of a particular gas or vapour, *i.e.* to detach completely one electron from it so that this electron possesses no kinetic energy as a result of the process (single ionization), always requires the *same* total absorption of energy whatever the nature of the ionizing source. Thus whether the atom is ionized by electron impact or by the absorption of radiation, the total ionization energy necessary to change it from the "normal" unexcited state to the ionized state is always the same. The long wave-length limit (threshold frequency) for the photo-electric effect in the vapour thus corresponds to the ionization potential for electron impact.

(b) "Single" ionization of an atom may be produced by absorption of the ionization energy from one or more of the following sources:—

1. Impact by an electron.
2. Impact by a positive ion.
3. Absorption of radiation (photo-electric ionization).
4. Impact by "normal" atoms (thermal ionization).

(c) If only *one* of the above sources is concerned, *e.g.* electron impact (about which we possess the most data), the absorption of the energy may take place in a single process or by stages; in this case by successive electronic collisions. If a partially ionized atom receives the extra amount of energy necessary to ionize before radiating the portion it has already received, ionization will result.

\* Communicated by Prof. S. R. Milner, F.R.S.

† With polyatomic molecules energy may be required first to dissociate the molecule.

(d) More than one of the above sources may be concerned in the ionization of an atom. Thus an atom may be partially ionized by absorption of radiation, and then the process may be completed by electron impact\*.

## 2. *Ionization by Positive Ion Impacts.*

The method of studying the ionization produced by *one* of these four methods alone must be by some form of discharge through the gas at low pressures. The conditions of the experiment must approximate to the following ideal conditions. Only the source of ionization, *e. g.* positive ion impact which is being studied, must contribute to the ionization of the gas, other sources being eliminated as far as possible by suitably designing the apparatus. We must also be able to distinguish between ionization produced by a single process and that produced by the cumulative effect of several collisions.

Assuming the foregoing principles concerning the energy exchanges in ionization, and given the ideal conditions stated above, we may expect the following result:—That for a positive ion accelerated through an electric field and striking an atom of the gas, in order just to ionize the atom its kinetic energy must be equal to the ionization energy of the atom. Thus if it has fallen unimpeded through an accelerating field of  $V$ , a singly-charged ion will have a kinetic energy of

$$Ve = \frac{1}{2}mv^2.$$

This accelerating P.D. of  $V$  reduced to volts is the ionization potential for positive ions. In a particular gas it should have the *same* value as the ionization potential for electron impact.

This ionization potential for positive ions should be independent of the *nature* of the ions, the effect depending only on their kinetic energy. These principles will apply only to the case where an atom is ionized by the impact of a single positive ion (possessing one positive charge) which has been accelerated unimpeded by a P.D. of  $V$  volts.

The case of positive ion impact may differ, however, from the case of electron impact in the following manner:—Though the kinetic energy of the accelerated positive ion is the same as that of an electron accelerated through a P.D. of the same value, the energy exchanges with the “struck”

\* H. D. Smyth and K. T. Compton, *Phys. Rev.* xvi. p. 501 (1920). (Iodine vapour.)

atom may not be so simple, the positive ion itself being a complex system. Thus the ionization potential might depend on the state of excitation of the positively-charged "striking" atom.

### 3. *Experimental evidence on Ionization by Positive Ions.*

To test the validity of these principles, we may examine existing evidence on impact ionization by positive ions, taking into account to what extent the experimental conditions approximate to the ideal conditions for the test.

(a) *High-speed Positive Ions.*— $\alpha$ -rays. Millikan\* has shown that ionization by  $\alpha$ -rays usually results in single ionization, more rarely in double ionization. Double ionization, i.e. detaching the second electron from the already ionized atom, of course requires a greater amount of energy than that necessary for single ionization. Assuming that in the flight of an  $\alpha$ -ray through hydrogen there is no loss of energy in non-ionizing collisions, and that each pair of ions produced levies a toll on the kinetic energy of the  $\alpha$ -particle of the same amount, and knowing the initial kinetic energy and the total number of ions produced, we may calculate the energy required to ionize a single molecule. This energy is that acquired by a single charge moving through 35 volts†. Since, however, much energy may be wasted in producing partial ionization or in useless kinetic energy of the ejected electron, we may regard this figure as a maximum value for the ionization potential for a singly-charged positive ion.

*Canal or Positive Rays.*—By applying a cross-field of a few volts behind a perforated cathode in a discharge-tube, Stark‡ used a galvanometer to measure the ionization current produced by the impact of the canal rays on the gas. In nitrogen at a pressure of 0.134 mm. he obtained signs of ionization when the cathode P.D. had a value of 500 volts. These conditions are very different from the ideal conditions necessary. At such high pressures the mean free path of the positive ion would be very small, and therefore we do not know to what extent when they produce ionization their kinetic energy is comparable with that derived from the total P.D. of 500 volts.

Moreover, in both these cases of ionization by high-speed positive ions it is probable that the mechanism is quite

\* Millikan, Phys. Rev. Dec. 1921, p. 456.

† Rutherford, 'Radioactive Substances and their Radiations,' p. 159.

‡ J. Stark, *Annalen der Physik*, 1906, p. 427. See also K. Glimme and J. Koenigsberger, *Zeits. für Physik*, 6, iv. pp. 276-297 (1921).



different from that operating with low-speed impact where the striking particle does not penetrate the atom.

In the case where the kinetic energy of the positive ion is great enough for it to penetrate the atom ( $\alpha$ -ray), the amount of ionization per cm. path increases as the speed of the ion decreases. The amount of perturbation increases with the time taken for the ion to cross the atom. Thus  $\alpha$ -rays produce most ionization near the end of their range. Glasson's\* experiments on ionization by cathode rays indicate a similar effect with high-speed electrons.

(b) *Ionization by Collision.*—Townsend† measured the current between two metal plates with different field-strengths between them, the negative plate being illuminated by ultra-violet light. For small distances between the plates the results could be readily explained on the assumption that the photo-electrons emitted by the negative plate (and the electrons they produced in the gas by ionization) when accelerated through the field produced  $\alpha$ -ions per cm. by collision with the molecules of the gas. For distances between the plates above a certain value he obtained currents which were larger than would be expected on the above simple theory, and ascribed this increase to ionization by positive ions which produced  $\beta$ -ions per cm.

For example‡, in hydrogen at 8 mm. pressure with a distance between the plates of .3 cm. and a field of 700 volts per cm. giving a P.D. of 210 volts between the plates, he obtained an increase ascribed to the action of positive ions. Thus positive ions falling through 210 volts in hydrogen at 8 mm. pressure ionize by impact. The M.F.P. of a positive ion would be very small at this high pressure, so that it could not obtain an unimpeded fall through more than a fraction of a volt. This suggests that the ionization produced may be due to (a) either successive collision or (b) an accelerated positive ion does not lose the whole of its kinetic energy on every collision, and so may acquire a velocity corresponding to a P.D. which is greater than that along its M.F. path.

(c) *Cathode Fall in Discharge-tubes.*—It is not yet clear whether the positive ions accelerated through the cathode fall of potential produce electrons (cathode rays) by impact with the molecules of the gas or with the metal or occluded gas of the cathode itself§. The values of the minimum

\* J. L. Glasson, *Phil. Mag.* (6) xxii. p. 647 (1911).

† J. S. Townsend, 'Electricity in Gases,' Chapter IX.

‡ *Ibid.* p. 317.

§ Ratner, *Phil. Mag.*, Dec. 1920, p. 785.

cathode fall of potential are very similar to those obtained for the minimum sparking potential in gases at the same pressure. In hydrogen their values are between 200 and 300 volts. In both these cases ionization by collision of positive ions becomes very important, but the corresponding pressures are so high that in no case will the accelerated positive ion fall unimpeded through the total P.D. Thus the essential condition for the test is not fulfilled in this case.

(d) *Positive Thermions from Glowing Filaments.*—Stark \* measured the current between a glowing carbon filament as anode and a metallic cathode 6 mm. apart in air at .22 mm. pressure with different applied P.D.'s. After obtaining saturation of the positive current for smaller values of the applied P.D., he obtained an increase of the current at 350 volts which he ascribed to the positive ions from the filament producing ionization in the gas. McClelland † obtained a similar result using an incandescent anode in air at .66 mm. pressure, when he found that an increase of current took place at 240 volts. In both these cases the pressure is so high that the P.D. between the two ends of the M.F.P. is only a small fraction of a volt.

The only experiments in which the necessary conditions have been at all fulfilled are the following three cases, in which, however, the positive ions were those emitted by glowing coated and uncoated filaments, so that their nature was not known exactly. Pawlow ‡ measured the ionization produced by positive thermions from coated filaments, when accelerated through small potentials, by Lenard's method. He obtained signs of ionization in hydrogen at as low as 10 volts, and found that the minimum potential at which ionization could be detected varied with the supply of positive ions, being smaller for a greater intensity of the source. He also found that positive ions were much less efficient in producing ionization than electrons accelerated through the same voltages. The fact that the minimum potential depends upon the original number of positive ions suggests ionization by successive collision. Franck and Eva v. Bahr § in similar experiments with air and hydrogen obtained signs of ionization in a gas at potentials below the ionization

\* Stark, *Annalen der Physik*, 1906, p. 427.

† McClelland, *Phil. Mag.* xxix. p. 362 (1915).

‡ Pawlow, *Proc. Roy. Soc.*, July 1914, p. 398.

§ Franck and Eva v. Bahr, *Verh. der Deuts. Phys. Gesell.* Jan. 1914, p. 57.

potentials for electrons in the gas. They concluded that there was no sharp ionization potential for positive ions in the gas, and also found that the minimum potential at which ionization could be detected was lower the greater the intensity of the source of positive ions. Horton and Davies\* made a thorough investigation of the ionizing properties of the positive ions emitted from an incandescent tantalum filament in helium. Their results indicated the production of fresh ions by collision of positive ions accelerated through 20 volts. Further investigation led to the view that the ionization produced was not due to the ionization of the gas molecules by direct positive ion impact, but to the bombardment of the walls of the ionization chamber by positive ions releasing  $\delta$ -rays. They conclude that the positive ions do not produce ionization when accelerated through potentials of 200 volts. Thus the only investigations satisfying the necessary conditions are to some extent contradictory.

#### 4. *Description of Apparatus.*

The following experiments were undertaken with the hope of obtaining more definite information about the conditions under which ionization is produced by low-speed positive ions. Other workers have used the positive ions from glowing filaments so that their nature was not definitely known. In the present work the nature of the ionizing positive ions was known with greater certainty. They were produced by electron impact in hydrogen, and the speed of the colliding electrons was great enough to dissociate the molecule on ionization. Thus the positive ions formed would be H-nuclei (protons). They were accelerated through hydrogen at very low pressure and their ionizing properties studied.

In figs. 1 and 2, F is a tungsten filament heated by a battery of 8 volts supplying a current of 2 to 3 amps. and insulated on paraffin-wax blocks. The filament leads are sealed into a glass tube, the end of which fits as a ground-glass stopper into the side tube B. With this arrangement, when the filament burnt out, it could be replaced more easily. The electrons from the glowing filament F are accelerated towards the nickel electrode A by the P.D. of V volts between the negative end of the filament and A. If V is greater than the ionization potential for electrons in hydrogen, ionization by electron impact occurs near to A, and the resulting positive ions are accelerated towards the filament by V. Some strike the filament, but some pass on

\* Horton and Davies, *Proc. Roy. Soc.*, March 1919, p. 333.

through the gauze  $G_1$ . These positive ions may be further accelerated by the P.D. of  $y$  volts between the gauzes, whence they pass into the ionization chamber  $G_2D$ , where the ionization they produce can be measured. The nickel gauzes  $G_1$  and  $G_2$  are of fine mesh, and are fitted on frames so that they do not touch the glass walls of the main tube. This lessens the possibility of a current leak across the glass.

Fig. 1.

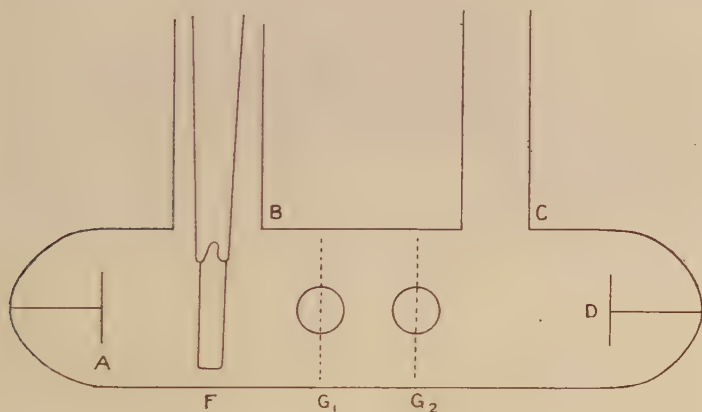
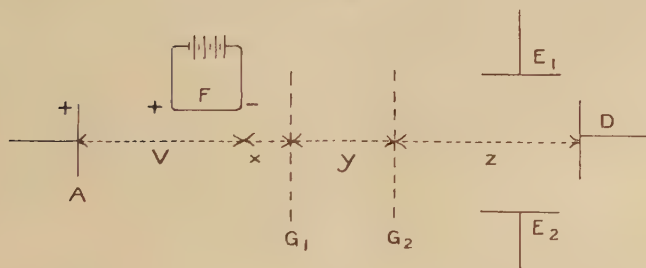


Fig. 2.



One set of wires in each gauze is set vertical and the other set horizontal so that the corresponding holes in the gauzes are opposite.  $E_1$  and  $E_2$  are side electrodes for using a cross-field to measure the ionization.

Before fitting, the tube was thoroughly cleaned and dried. After fitting to the supply tube, it was exhausted as much as possible by an automatic mercury pump, the glass walls



being heated to drive off occluded gases, and the filament was made white-hot. The hydrogen was prepared by electrolyzing a solution of baryta in distilled air-free water. The prepared gas was then allowed to stand for several days over  $P_2O_5$ . A gold-leaf tube was fitted to eliminate mercury vapour from the ionization tube. Pressures were measured by a sensitive McLeod gauge. To keep the pressure as constant as possible and thus minimise the pressure-change due to the "clean-up" effect of the filament burning in hydrogen, bulbs of large capacity were fitted in the delivery tube to the ionization apparatus. The ionization currents were measured by a sensitive quadrant electrometer, and all the batteries were insulated by paraffin-wax.

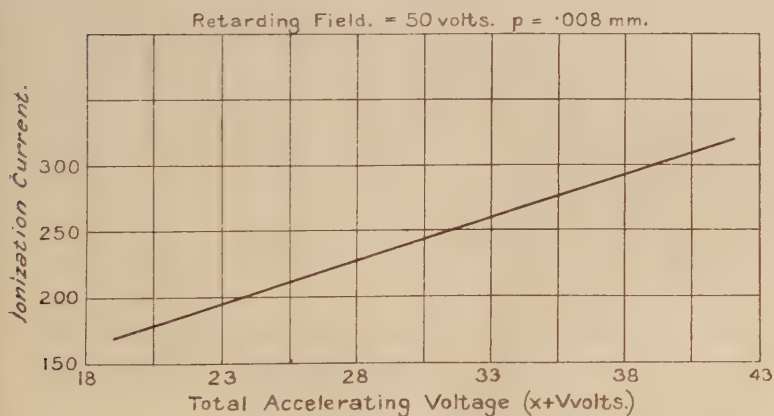
*Summary of Results.*—This apparatus showed some faults of design which were afterwards remedied in a new apparatus. It was found, however, that positive ions produced ionization in the hydrogen when accelerated through 19 volts, which was the minimum accelerating potential possible. Consider first the production of the ionizing positive ions. To produce these in quantity it was found that the arcing potential  $V$  must be greater than 16 volts. The pressure of the gas was tried at values between .005 mm. and .01 mm. of mercury. These pressures were chosen because they were about the lowest at which both the positive-ion current and the resulting ionization current were measurable on the electrometer. The pressure must be low enough so that the M.F.P. of the positive ions produced near to  $A$  will be greater than the distance  $AG_2$ . Thus most of the positive ions will not collide with the gas molecules before reaching the ionization chamber  $G_2D$ . On the other hand, if the pressure is too low the M.F.P. of the electrons in the gas will be much greater than  $FA$ , so that none of them will collide with the molecules before reaching  $A$ . The positive-ion current had values varying from  $10^{-9}$  amp. upwards. It increased with the arcing potential  $V$ , the pressure of the gas, and the filament current which controlled the supply of the thermo-electrons from the filament. The supply of positive ions from this low-voltage arc in hydrogen for larger values of  $V$  showed much unsteadiness, and thus it was difficult to compare the ionization produced with different accelerating potentials as the ionizing current itself was not sufficiently constant.

A more serious drawback was due to the fact that the filament itself emitted positive ions. An attempt was made to cut off this positive thermionic current by fitting a

nickel-foil screen partly round the filament, but this was found unsatisfactory, apparently owing to the diffusion of the ions. With the negative end of the filament connected directly to the gauze  $G_1$  so that  $x=0$ , it was found that many thermo-electrons shot out into the space between the gauzes. To prevent this,  $G_1$  was made negative with respect to the negative end of the filament, a retarding P.D. of  $x$  volts being applied. With  $x=3$  volts as a minimum, this effect could no longer be detected.

The ionization produced was measured by Lenard's method, using the gauge  $G_2$  as a collecting-plate instead of D to shorten the distance the positive ions had to travel before ionizing by collision. A retarding field of 50 volts for positive ions was applied between  $G_1$  and  $G_2$ . The arcing potential  $V$  was kept constant, and  $x$  increased to increase the total accelerating P.D. of  $x+v$  volts. The ionization current plotted against the total accelerating voltage is shown by a typical curve in fig. 3. The readings were taken

Fig. 3.



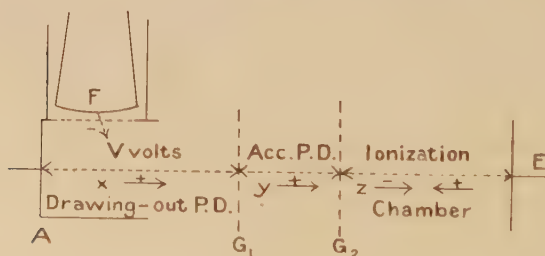
in rapid succession to avoid any alteration in the ionizing current. Values of the accelerating voltage below 19 volts were not possible, and readings to repeat were difficult to obtain because of the variation in the ionizing current which depended upon three variables, the temperature of the filament, the pressure of the gas, and also to some degree on the value of  $x$ , the "drawing-out P.D." A second method was tried to detect ionization by applying a cross-field of

4 volts between the side electrodes  $E_1$  and  $E_2$ , and putting both  $G_2$  and  $D$  to earth.  $E_1$  was maintained at a potential of  $-4$  volts, and  $E_2$  connected to the electrometer. Since  $E_2$  was positive with respect to the electrode  $E_1$ , it should collect the *negative* ions produced by collision. It was found, however, that  $E_2$  was always charged up *positively* by an amount which increased with the accelerating P.D. of the positive ions. The effect is probably due to the formation of a positive space-charge in the ionizing chamber. This positive charge deflects the incoming positive ions to the side electrodes.

### 5. Description of Apparatus 2.

To obtain more definite results, two improvements on the old apparatus were desirable. The positive-ion current from the filament itself must be eliminated. It was also desirable to work at much lower accelerating voltages to detect the potential at which ionization sets in. A diagram of the second apparatus is shown in fig. 4. The side electrodes

Fig. 4.



$E_1$  and  $E_2$  were omitted and the end electrode  $E$  increased in area. The tungsten filament  $F$  was placed in a side tube to cut off the positive ions given off by the filament itself. The filament was surrounded by a nickel-foil screen, which rested on the top of the cylinder  $A$ .

Electrons from  $F$  were accelerated by the arcing potential  $V$  into the nickel cylinder  $A$  through the gauze opening, and there produced positive ions in the hydrogen by collision. A P.D. of  $x$  volts is applied between  $A$  and  $G_1$  to draw out the positive ions, which, passing through the gauze  $G_1$ , are then accelerated by a P.D. of  $y$  volts between  $G_1$  and  $G_2$ . A retarding P.D. for positive ions of  $z$  volts is applied in the ionization chamber between  $G_2$  and  $E$ .



The different currents in the apparatus were measured as follows :—

(a) The filament was heated by an insulated 8-volt battery with resistances. The current which was usually about 3.5 amps. was measured by an ammeter.

(b) The thermionic current between F and A, which was always of the order of a few milliamps., was measured by a Paul single-pivot galvanometer with shunt. The constancy of this current rather than its absolute value was the reason for measuring it. If this current had a constant value, it indicated a constancy of conditions (pressure of gas and filament temperature) in the apparatus.  $V$  was measured between the negative end of the filament and the cylinder. It had a minimum value of about 16 volts in order to produce a satisfactory supply of positive ions.

(c) The positive-ion current leaving the cylinder for the gauzes to produce ionization in  $G_2E$  was measured by a suspended magnet galvanometer, and was usually of the order of a few microamps. The galvanometer was connected between the cylinder A and the insulated battery giving  $x$  and  $y$ , and thus measured the total positive current leaving the cylinder. To compare the amount of ionization produced by a stream of positive ions accelerated through different voltages, it was essential that this current should keep constant. The positive ions were drawn out of the cylinder by the field  $x$ , which penetrated inside the cylinder. This positive current varied with the original thermionic current, the drawing-out P.D.  $x$ , and the pressure of the gas.

It was found that for small values of  $x$  and large values of  $V$ , especially with a heavy thermionic current, the current leaving the cylinder was *negative* although the P.D.  $x$  opposed a negative current. The filament was screened from the gauze  $G_1$  by the nickel-foil screen so that no electrons accelerated by  $V$  could shoot through directly against  $x$  towards the gauzes. With smaller values of  $V$  the current leaving the cylinder was small but positive, and was probably a mixture of positive and negative currents with a preponderance of the former. The effect was probably due to the formation of a negative space-charge (inside the cylinder A) which repels incoming electrons to the gauzes and to the ordinary diffusion of electrons. It was impossible to be certain that the positive-ion current did not contain some negative current against the field  $x$  unless the value of  $x$  was greater than  $V$ . These positive and negative currents could not be measured separately. The field due to the space-charge could not be greater than the field

producing it. Thus, since  $V$  cannot be less than 16 volts and  $x > V$ ,  $x > 16$ , which sets a minimum value to the total accelerating field of  $x + y$ .

(d) The positive-ion current entering the ionization chamber was measured for different values of  $x$  and  $y$  and for different pressures (the retarding field being kept at zero) by measuring the rate of charging up of the electrode E connected to the electrometer.

For higher pressures (1 mm. Hg) the positive-ion current reaching E was only a small fraction—about one-tenth—of the original positive-ion current leaving the cylinder.

As the pressure was diminished, a greater proportion reached E, indicating that at higher pressures many of the ions were stopped by collision with the molecules. The whole of the batteries, leads, and measuring instruments were insulated on paraffin-wax blocks, and tests carried out to ensure that none of the measurements of the different currents were affected by spurious leaks.

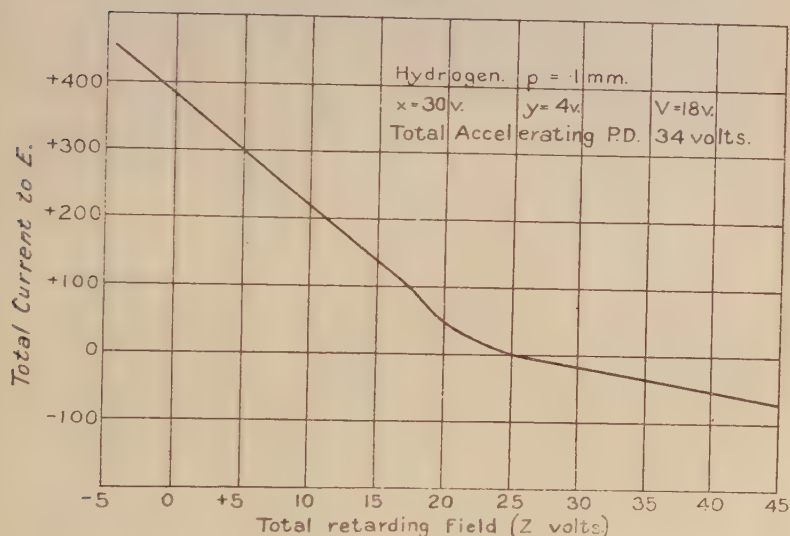
*Detection of Ionization.*—The first method employed to detect ionization by collision by the positive ions was to take fixed values of  $x$  and  $y$  and to measure the charging up of E as the retarding field  $z$  was increased gradually. No precautions were necessary to distinguish between ionization and radiation produced in  $G_2E$ . In the case of *electron* impact the collecting electrode is negative with respect to the gauze, and so it may charge up positively by releasing electrons under the influence of the radiation, or it may charge up positively as it collects the positive ions. In the present case, since E is positive with respect to  $G_2$ , radiation will not release electrons from E, which will collect the negative ions produced on ionization. The ionization currents were measured by the steady potential assumed by the electrometer quadrants when connected to earth across a high-resistance leak. The values of  $z$ , i. e. the P.D. between  $G_2$  and E, were corrected for this potential assumed by E.

The type of curve obtained plotting the current to E against an increasing retarding field  $z$  is shown in fig. 5. Great difficulty was experienced in keeping the positive ionizing current sufficiently constant so as to render the results comparable for different values of  $z$ .

For small values of  $z$  the current (potential assumed by E) was *positive*, but gradually diminished as  $z$  increased until for a certain value of  $z$  it became negative, further increase of  $z$  resulting in an increase of the negative current. This

"cross-over" potential is shown in fig. 5 at 25 volts. The effect of increasing the thermionic current and so the positive ionizing current is to shift the graph along to the right so that the cross-over potential is increased. These facts can be explained readily by the fact that the incoming positive ions ionize by collision. The current to E is thus made up of two currents—the positive ionizing current and the negative current of the negative ions produced. When  $z$  is sufficiently large, this negative electron current is sufficient

Fig. 5.



to swamp the positive current retarded by  $z$  and by collision with the gas molecules. *In this manner definite evidence of ionization by positive ions accelerated through potentials as low as 18 volts has been obtained.*

Other ionization tests were carried out with the retarding potential  $z$  of constant value and greater than the minimum value of  $x + y$ , the total accelerating P.D. Table I. illustrates the relation between the positive ionizing current and the negative ionization current for different applied P.D's.



TABLE I.

Total acc. P.D. ( $x+y$ ). (Volts).	Current +ive ionizing leaving cylinder. (Scale Divns.). $C_1$ .	Ionization current. [ $10^{-10}$ amp.]. $C_2$ .	$C_1/C_2$ .
36	+50	9	5.6
"	+100	15	6.7
92	+60	10	6-
"	+120	20	6
"	+145	23	6.3
"	+290	60	4.8

Hydrogen .....  $p=0.02$  mm. Hg.  $V=18$  volts.  $z=100$  volts.

The positive ionizing current was varied by varying the filament current. The results show that the amount of ionization is proportional to the ionizing current. The former current collected under a field of 100 volts is probably increased by the fact that the original electrons released by the positive ions themselves produce some fresh ions by collision. By obtaining the ratio of the two currents we can estimate a maximum value for the efficiency of the positive ions as ionizers. The ratio of the ionization current to the ionizing current for the results in Table I. is about  $1/130$ . Thus of at least 130 positive ions reaching the ionization chamber  $G_2E$ , only *one* ionizes a molecule of hydrogen. Electrons accelerated through the same voltage and at the same pressure in hydrogen would produce about one positive ion per ionizing electron\*. Hence when moving with these low velocities, the efficiency of an electron is much greater than that of the positive ion in producing ionization by collision. Most of the energy of the positive ions is lost probably in non-ionizing collisions.

### *Summary.*

An attempt is made to formulate the conditions governing the exchange of energy when an atom is ionized by impact or by the absorption of radiation. This is applied to the case of ionization by positive-ion impact with the conclusion that the ionization potential for positive-ion impact in a gas

\* J. B. Johnson, Phys. Rev. 1917, p. 609.

should be the same as that for electron impact. Results of previous workers show wide disagreement in the value of the minimum accelerating P.D. necessary for positive ions to produce ionization.

Two types of apparatus are described, the positive H-ions being produced first by electron impact in hydrogen. The peculiar difficulties of the experiment made it impossible to test for ionization produced by positive ions accelerated through less than 18 volts, and, as the ionizing current itself depended upon three variable factors, it was more difficult to obtain comparative observations. The results indicate that positive H-ions produce ionization in hydrogen when accelerated through P.D.'s. as low as 18 volts, and that they are much less efficient in producing ionization than electrons under similar conditions.

In conclusion, I desire to thank Prof. Milner, F.R.S., who proposed the problem, for his kindly interest and advice.

Sheffield University,  
July 31st, 1922.

LXXI. *On the Partition of Energy.*—Part II. *Statistical Principles and Thermodynamics.* By C. G. DARWIN, F.R.S., Fellow and Lecturer of Christ's College, Cambridge, and R. H. FOWLER, Fellow and Lecturer of Trinity College, Cambridge\*.

### § 1. *Introduction and Summary.*

IN a previous paper† we have developed a method of calculating the partition of energy in assemblies containing simple types of quantized systems and free molecules. In this method advantage is taken of the multinomial theorem, which makes it possible to obtain integrals expressing accurately the various average values concerned in partition problems, and then the integrals are easily evaluated asymptotically. The "fluctuations" can also be readily found, and from them it can be shown that the possession of these mean values is a "normal" property of the assembly in the sense used by Jeans‡. This method has the advantage of obtaining directly the

\* Communicated by the Authors.

† Phil. Mag. vol. xliv, p. 450 (1922).

‡ Jeans, 'Dynamical Theory of Gases,' *passim*. Average and most probable values are of course in practice the same.

average properties of the assembly, which are, on any statistical theory, those which experiment determines, instead of the most probable values, as is usually done. It can also be carried out simply and rigorously without the use of Stirling's theorem, and thus provides satisfactory proofs of all the usual partition laws, including Maxwell's Distribution Law.

In this discussion the partition laws were all obtainable without any reference to thermodynamical ideas, in particular without any mention of entropy. This we claim as an advantage. But a great deal of work has been done on partition laws, in which the idea of entropy has played a leading part; so that, for this if for no other reason, it is fitting to examine its position in our presentation of statistical theory. But the power of our method on the statistical side invites a somewhat more general review of the fundamental connexion between classical thermodynamics and statistical mechanics both of classical dynamics and the quantum theory. In the former work we were content with purely statistical results, and identified the temperature scale simply by the perfect gas laws; here we attempt a more strictly logical development, and *prove* the laws of thermodynamics for assemblies composed of systems of a fairly general type, and, by linking on to Gibbs' work, also for general systems which obey the laws of classical mechanics.

After summarizing our previous results in § 2, we pass in § 3 to a comparison between the empirical temperature in thermodynamics and the parameter which acts as temperature in our previous work. In §§ 4, 5, 6, we make a critical study of the usual presentation of entropy in statistical theory. This is ordinarily introduced by means of Boltzmann's Hypothesis, which relates it to probability, and, though no objection can be made to much of the work based on this hypothesis, it appears to us that the development is often marred by somewhat loose reasoning. Though much that we here say is general and not at all dependent on our special methods of treatment, yet it has been far easier to examine the validity of the arguments on account of the way in which it is possible to combine assemblies together at will. In consequence of this discussion we are led, in § 7, to a presentation of entropy which is very closely related to that of classical thermodynamics, which frees it from the combinatory complications with which it is normally associated and brings it back to direct dependence on the partition



functions which form the basis of our method. In § 8 the definition is considerably simplified mathematically by replacing the "entropy" by the "characteristic function" as the basal thermodynamic quantity. In § 9 we show that for an assembly in a temperature bath our method is exactly equivalent to Gibbs' use of his "canonical ensemble," and in § 10 we consider briefly the possibility of inverting the argument so as to obtain information about the elementary states from thermodynamic data.

## § 2. Summary of our previous paper.

It was shown in the previous paper how the partition of energy could be evaluated for various types of assembly. Those chiefly treated were quantized systems, for which the energy was sole variable; but it was also shown how to apply the method in the case of a perfect gas, where both energy and volume are variable. It is easy to see that the method is applicable in considerably more general cases. The partition of energy could be evaluated when any of the types enumerated were mixed together, the essential point of the method being the existence of a certain function, the partition function, for each type of system. By means of these functions all the rather tiresome combinatory expressions can be very easily dealt with so as to obtain mean values, and also the fluctuations about those mean values.

The partition function of a system—which with a different notation is the "Zustandsumme" of Planck—is constructed as follows. The possible states of the system may be divided into cells; these cells are fixed and finite for quantized systems, but for the systems of classical mechanics must ultimately tend to zero in all their dimensions. Associated with each cell is a weight factor, determined by the usual statistical principles. The weight of any cell of a system obeying Hamiltonian equations is proportional to its extension. The relative weights of the cells of a quantized system are determined by Bohr's Correspondence principle, and the weights are all assigned definite magnitudes by the convention that a simple quantized cell shall have unit weight. For consistency in physical dimensions the cells for Hamiltonian systems are divided by the appropriate power of  $h$  to give their weight. Associated with any cell there is a definite energy, depending on the cell and on certain external parameters  $x_1, x_2, \dots$ ; this last is a slight extension of our previous paper, which must be made so as to deal with questions of external work. Then, if  $p_r$  is the

weight and  $\epsilon_r$  the energy in the  $r$ th cell, we define as the partition function

$$j = \sum_r p_r S^{\epsilon_r},$$

summed over all the cells. The partition function is thus a function of  $\mathfrak{S}$ ,  $x_1, x_2, \dots$ . For systems of classical mechanics the extensions of the cells, that is the  $p$ 's, all tend to zero, and the sum is replaced by an integral.

As an example of the systems treated we may mention first Planck's line vibrator, which can take energy in multiples of  $\epsilon$ . This has the partition function

$$\frac{1}{1 - \mathfrak{S}^\epsilon} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (2.1)$$

More important is the free monatomic molecule. If it is of mass  $m$  and is confined in a volume  $V$ , its partition function is

$$\frac{(2\pi m)^{3/2} V}{h^3 (\log 1/\mathfrak{S})^{3/2}} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (2.2)$$

The partition function of a diatomic molecule is simply given by multiplying (2.2) by the partition function corresponding to the quantized rotations (assuming that the atoms cannot vibrate relatively to one another).

Now suppose that we have any number of types of systems together in an assembly: let there be, say,  $M_A$  of type A with partition function  $f_A$ . Then it was shown that the average energy among the systems of this type was given by

$$\bar{E}_A = M_A \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log f_A, \quad \cdot \cdot \cdot \cdot \cdot \quad (2.3)$$

where  $\mathfrak{S}$  is uniquely determined in terms of  $E$  the total energy by

$$E = \sum_A M_A \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log f_A. \quad \cdot \cdot \cdot \quad (2.4)$$

It is easy to show that  $\mathfrak{S}$  is always less than unity. The average number of systems A in the  $r$ th cell is also easily found, and is

$$\bar{a}_r = M_A p_{A,r} \mathfrak{S}^{\epsilon_{A,r}} / f_A. \quad \cdot \cdot \cdot \quad (2.5)$$

In connexion with the relation of entropy to probability, we must also recapitulate some of the work from which the above results were derived. The statistical state of an

assembly, say of two groups A and B, M and N in number respectively, is specified by giving sets of numbers  $a_0, a_1, a_2, \dots, b_0, b_1, b_2, \dots$ , where  $a_r$  is the number of the A's which lie in the  $r$ th cell. Suppose that this cell has a weight factor  $p_r$  and that the  $s$ th cell for a B has a weight factor  $q_s$ : then the fundamental basis on which the whole of statistical theory rests gives an expression,

$$\frac{M!}{a_0! a_1! \dots} p_0^{a_0} p_1^{a_1} \dots \times \frac{N!}{b_0! b_1! \dots} q_0^{b_0} q_1^{b_1} \dots \quad (2.6)$$

for the number of "weighted complexions" corresponding to that specification. If this number is divided by the total of all the weighted complexions, which we call C, which correspond to any distribution of  $a$ 's and  $b$ 's consistent with the same total energy, then this ratio is the proper measure of the probability of the specification, and must be used in calculating the expectation of any quantity. It was shown in the former paper that C and the associated averages can be expressed as contour integrals (exact for quantized systems) which lead asymptotically to the formulæ (2.3), (2.5).

### § 3. Temperature.

In considering the connexion between statistical theory and the principles of thermodynamics, we must begin by correlating the ideas of temperature in the two theories. Throughout our former paper we have treated the parameter  $\mathfrak{S}$  as of the nature of the temperature, and it is here of some importance to observe that  $\mathfrak{S}$  has precisely those properties which must be postulated of the "empirical temperature" when the foundations of thermodynamics are rationally formulated\*. The basal fact of thermodynamics is that the state of two bodies in thermal contact is determined by a common parameter which is defined to be the empirical temperature. The temperature scale is at this stage entirely arbitrary, and any convenient body whatever may be chosen for thermometer. On the statistical side we have shown that when two assemblies can exchange energy so that there is one total energy for the two together, then their states are defined by a common parameter  $\mathfrak{S}$ . The analogy is exact, and we are therefore logically justified in identifying  $\mathfrak{S}$  with the empirical temperature in precisely the thermodynamical sense.

\* See, for instance, Max Born, *Phys. Zeit.* vol. xxii. pp. 218, 249, 282 (1921).

Since we may take any body for our thermometer by which to measure the temperature scale, we may if we like at once define the absolute temperature of statistical theory as proportional to the pressure in a body of perfect gas at constant volume. Now if there are  $P$  molecules in volume  $V$ , it follows from almost any theory that

$$p = \frac{P}{V} \frac{2}{3} \bar{e}_{\text{kin.}}, \quad . \quad . \quad . \quad . \quad (3.1)$$

where  $\bar{e}_{\text{kin.}}$  is the mean kinetic energy of translation of a molecule. In terms of  $\mathfrak{S}$  we have by (2.2) and (2.3)

$$P \bar{e}_{\text{kin.}} = \frac{3}{2} \frac{P}{\log 1/\mathfrak{S}};$$

and so we must have

$$\log 1/\mathfrak{S} = 1/kT, \quad \mathfrak{S} = e^{-1/kT}, \quad . \quad . \quad . \quad (3.2)$$

where  $k$  is a universal constant.

This appeal to the properties of an ideal substance is, however, not quite satisfactory. It is avoided in thermodynamics, where the absolute temperature is defined in connexion with the Second Law. Now we wish to show how our theorems lead to the laws of thermodynamics, and so we must not postulate a knowledge of absolute temperature, but must only consider it in connexion with entropy. Our development of the Second Law will not of course have the complete generality for classical systems of such treatment as Gibbs' (though we have later extended it to his case), but still it will suffice to deal with assemblies as general as those that have been used by most writers who have deduced special thermodynamical conclusions from statistical premises.

#### § 4. *The usual presentation of Entropy.*

Entropy is usually introduced into statistical theory by means of Boltzmann's Hypothesis relating it to probability. This hypothesis is based in general on the fact that, on the one hand, an assembly tends to get into its most probable state, while, on the other, its entropy tends to increase, and so a functional relation between the two may be postulated. The general line of argument is somewhat as follows\* :—

We can assign the numerical value  $W_1$  for the probability of the state of any assembly. If we have two such assemblies

\* Planck's classical work on Radiation Theory is a representative example of the use of the argument here quoted.



which are quite independent, then by a fundamental principle of probability, the joint probability is the product of the separate probabilities ; that is,

$$W_1 W_2 = W_{12} \dots \dots \dots (4.1)$$

On the other hand, the joint entropy is the sum of the separate entropies, and so

$$S_1 + S_2 = S_{12} \dots \dots \dots (4.2)$$

Then to satisfy the functional relationship we must have

$$S = k \log W, \dots \dots \dots (4.3)$$

$k$  being a universal constant. Next, to evaluate  $W$ , a definition is made of "thermodynamic probability" as the number of complexions corresponding to the specified state : this is made a maximum subject to the condition of constant energy, and the maximum of  $k \log W$  is equated to the entropy  $S$ , which is then shown by examples to be the entropy of thermodynamics. Observe that there are two separate processes involved : in the first the determination of the maximum fixes the most probable state of the assembly by itself. In the second the assembly is related to the outside world by determining its entropy ; and then the absolute temperature scale is introduced by the relation  $\partial S / \partial E = 1/T$ .

Now there is much to be criticized in this argument. In the first place there is a good deal of vagueness as to what is happening. For the addition of entropies can only be realized by some form of thermal contact \*, and is then only in general true when the temperatures are equal ; and both these conditions require that the assemblies shall not be independent. So it is only possible to give a meaning to (4.2) by making (4.1) invalid. Again, without more definition the *probability* of a state is quite ambiguous : for example, we can speak of the probability of one particular system having, say, some definite amount of energy, and for independent assemblies (4.1) will be true of this type of probability, but it will have no relation whatever to entropy. This objection is supposed to be met by the definition of "thermodynamic probability" ; but that is a large integer and not a fraction, as are all true probabilities, and so (4.1) cannot be maintained simply as a theorem in probability.

\* There is perhaps an exceptional case, that of radiation, worked out by Laue and cited by Planck ('Radiation Theory,' ed. 3, p. 116) ; but a general theorem must be generally true.

Now it is established that actually the "thermodynamic probability" does lead to the entropy, and so we must consider how it is to be interpreted in terms of true probability. It is clear that the "thermodynamic probability" must be divided by the total number of admissible complexions, and that when we consider an assembly of given energy this number is  $C$ . In so far as we have to calculate the most probable state, only ratios are concerned and the denominator is immaterial, for we only have to deal with the equation \*

$$S' - S'' = k \log (W'/W'') ; \quad . \quad . \quad . \quad (4.4)$$

there is no difference between using "thermodynamic" and true probability. But when we attempt to determine the value of the entropy itself by (4.3), we shall in all cases find that when  $W$  is a true probability the maximum value gives always  $S=0$ —a trivial determination of the arbitrary constant in the entropy. This result may be verified for any of the examples of the former paper. We have merely to substitute values for the  $a$ 's and  $b$ 's of the specifications, and make use of Stirling's theorem in the form

$$\log (x!) = x \log x - x. \quad . \quad . \quad . \quad (4.5)$$

This is an approximation which is known by experience to suffice in entropy calculations. The zero value of  $S$ , roughly speaking, expresses the fact that a "normal" distribution is so enormously more probable than any other that by comparison it is certain, and so for it  $W=1$ .

It is thus clear that the straightforward process is useless, and we must consider how it is to be modified so as to retain the relation with true probability while giving the actual value of the entropy—in effect we must find a way of justifiably omitting the denominator  $C$ . As long as we consider the whole assembly this is impossible, for  $C$  depends on  $\mathfrak{S}$  and cannot be regarded as an ignorable constant when changes of temperature are contemplated. But if instead we consider the entropy of a group of systems immersed in a temperature bath, it becomes simple. Take, for example, a group of  $M$   $A$ 's—systems of the general quantized type described in § 2—and suppose them immersed in a bath of a very much larger number of  $B$ 's. We can now define the entropy of the  $A$ 's when their specification is  $a_0, a_1, \dots$  as  $k$  times the logarithm of the probability of that specification. In calculating

\* See Ehrenfest and Trkal, Proc. Acad. Amsterdam, vol. xxiii. p. 162 (1921).

this probability we are indifferent about the distribution among the  $B$ 's, so we sum the complexions involving all values of the  $b$ 's consistent with the selected values of the  $a$ 's. Then

$$W(a_0, a_1, \dots) = \left( \frac{M!}{a_0! a_1! \dots} p_0^{a_0} p_1^{a_1} \dots \right) \left( \sum_b \frac{N!}{b_0! b_1! \dots} q_0^{b_0} q_1^{b_1} \dots \right) / C, \quad (4.6)$$

where the  $a$ 's may have any values (which do not involve a greater total energy than that of the whole assembly), while  $\sum_b$  denotes summation over all different values of the  $b$ 's such that

$$\sum_s \eta_s b_s = E - \sum_r \epsilon_r a_r,$$

and of course, as always,  $\sum_r a_r = M$ ,  $\sum_s b_s = N$ . Now, provided that  $N$  is much larger than  $M$ , the factor

$$\left( \sum_b \frac{N!}{b_0! b_1! \dots} q_0^{b_0} q_1^{b_1} \dots \right) / C$$

will be practically independent of the  $a_r$ 's and of the energy of the group of  $A$ 's—that is to say, it may be taken as constant and omitted from the calculation, and we are left with the “thermodynamic probability” as the only variable part.

It is only in this sense that a strict meaning can be assigned to Boltzmann's Hypothesis; and it is of the greatest interest that the conditions under which it has meaning correspond exactly to the conditions of the “canonical ensemble” of Gibbs, as will be shown later. But, even so, it is not a very convenient expression, for we must always suppose that the assembly is a part of some much larger one, whereas the expression for the entropy is purely a function of the group and the temperature. It is therefore more convenient to abandon the use of the principles of probability and to define the entropy as  $k$  times the logarithm of the number of complexions (weighted if necessary). We shall call this the kinetic entropy. This number of complexions has the multiplicative property (4.1), but now in virtue of its own combinatory formula and not of an appeal to an inapplicable probability theorem. The new definition does not appear to have the same simplicity as the old, but that is only because in the old the necessity for a detailed definition of what is meant by probability was concealed. It would appear that

some such argument as this is necessary to justify the use of "thermodynamic probability," the quantity used with success by so many writers.

The argument of this section has really been dealing entirely with the junction of assemblies which had the same temperature; it may be more conveniently visualised as dealing with the separation of an assembly into parts which are thereafter isolated from one another. Actually of course our work must include the fact that entropy has the property of increasing when assemblies at different temperatures are joined. We have not yet had cause to discuss this, as we have so far been mainly criticizing theories which were developed by considering only assemblies of the same temperature.

### § 5. *Entropy as a non-fluctuating quantity.*

The kinetic entropy as defined above is a fluctuating quantity, whether we find it for the whole assembly or for a part. On the other hand, the entropy of thermodynamics is a function of the state of the assembly and must be regarded as constant, and we must see how the two may be best related. Now we cannot get away entirely from the question of fluctuations, but we can conveniently simplify the definition so as to dissociate them from the entropy. Consider an assembly composed of A's and B's. At every moment its state is specified by the values of  $a_0, a_1, \dots b_0, b_1, \dots$ , and these numbers all fluctuate, and with them the energy  $E_A$  and the kinetic entropy  $S_A$ . But if we want to treat of the entropy of the A's as opposed to that of the B's, we must suppose the A's to be suddenly isolated. After the isolation they will have a certain definite energy determined by the chance state at the moment of isolation, and this energy will determine the temperature and so the thermodynamic entropy. So, to define a function representing the thermodynamic entropy, it is most reasonable to choose some simple non-fluctuating function of the state of the whole assembly; we can then allow for the fluctuations in the entropy of its parts by imagining them suddenly isolated, and calculating their entropies from the energies they chance to have at the moment of isolation on the same principle as was previously done for the whole assembly. There are several suitable definitions—for example, we can use the total number of the complexions, or the average number, or the maximum



number, in each case attributing to the  $A$ 's the amount of energy they had at the moment of isolation. Now if these quantities are calculated, it will be found that, to the approximation (4.5), they all have the same value. This value is easiest to find for the maximum number. It is unnecessary to take an assembly of systems of more than one type, as we have seen that the additive property will hold. We have

$$S/k = \log M! - \sum_r \log \bar{a}_r! + \sum_r \bar{a}_r \log p_r.$$

We must here make the unjustified application of Stirling's theorem to numbers some of which will undoubtedly be small; it should be possible to justify the process, but we shall not do so. Then, making use of (2.1), (2.5), we have

$$S/k = M \left[ \log f - \log \mathfrak{A} \cdot \mathfrak{A} \frac{\partial}{\partial \mathfrak{A}} \log f \right], \quad . \quad . \quad (5.1)$$

$$= M \log f + E \log (1/\mathfrak{A}), \quad . \quad . \quad . \quad (5.2)$$

since

$$E = M \mathfrak{A} \frac{\partial}{\partial \mathfrak{A}} \log f.$$

Equations (5.1) and (5.2) remain equally true for a group of free molecules to the same approximation. This formula for  $S$  is the direct consequence of Boltzmann's Hypothesis, and  $S$  has the necessary additive property for combining the parts of the assembly. Moreover, it agrees completely with the entropy of thermodynamics in all cases where they can be compared: this agreement justifies our use of (4.5) in these calculations. But it is indifferent whether we define the entropy as the total, average, or maximum number of complexions, and (4.5) is always inexact; it is therefore unsatisfactory to make the formal definition of non-fluctuating entropy in any of these ways. Now (5.1) and (5.2) give *precisely* the thermodynamic expressions in all comparable cases, and this suggests a direct definition in terms of partition functions. We may thus suppose that the combinatory processes are correctly looked after by the partition functions, and may define the entropy by either of the relations (5.1) or (5.2). Pending its formal identification with the entropy of thermodynamics, we shall describe it as the "statistical entropy."

§ 6. "*The increasing property*" of *Entropy*.

We have now obtained a quantity  $S_{st.}$ , the statistical entropy, which is evidently related to the entropy of thermodynamics  $S_{th.}$ , but we must examine what right we have to make the identification complete. By its definition (5.1),  $S_{st.}$  has the additive property for separation, and we can easily show that for junction it has the property  $S_1 + S_2 < S_{12}$ , which may be called the *increasing property*.

Consider the special case of two assemblies, and suppose that in their junction only changes of temperature are concerned—not of volume or any other parameter. We shall also simplify by supposing that in each assembly there is only one type of system, different for the two. As we do not intend to base our final result on the present paragraph, this will be general enough. By definition, for the first assembly before junction the entropy is given by

$$S_{st.}'/k = M' \log f'(\mathfrak{S}') - E' \log \mathfrak{S}'.$$

Now when the energy  $E'$  is given, the temperature  $\mathfrak{S}'$  is determined by (2.4), and this is equivalent exactly to the condition that  $S_{st.}'$  should be a minimum for given  $E'$ . So, if  $\mathfrak{S}$  has any value different from  $\mathfrak{S}'$ ,

$$S_{st.}'/k < M' \log f'(\mathfrak{S}) - E' \log \mathfrak{S}.$$

Similarly,

$$S_{st.}''/k < M'' \log f''(\mathfrak{S}) - E'' \log \mathfrak{S},$$

if  $\mathfrak{S}$  is different from  $\mathfrak{S}''$ , the temperature of the second assembly. It follows that unless  $\mathfrak{S}' = \mathfrak{S}'' = \mathfrak{S}$  we have

$$(S_{st.}' + S_{st.}'')/k < M' \log f'(\mathfrak{S}) + M'' \log f''(\mathfrak{S}) - E \log \mathfrak{S},$$

where  $E' + E'' = E$ , the energy of the joint assembly. Now with a suitable choice of  $\mathfrak{S}$  this is  $S_{st.}/k$ , where  $S_{st.}$  is the entropy of the joint assembly after combination; so we have proved that (when no volume or other such changes take place)

$$S_{st.}' + S_{st.}'' < S_{st.}, \quad (E' + E'' = E),$$

unless the initial temperatures are equal, in which case

$$S_{st.}' + S_{st.}'' = S_{st.}.$$

Thus statistical entropy has the increasing property.

It is often taken for granted that if we can find a function of the state which has the increasing property, then that function must be the entropy: this assertion tacitly underlies Boltzmann's hypothesis. But the identification of  $S_{st.}$  with  $S_{th.}$ , the entropy of thermodynamics, cannot be established in

this way because the function  $\Sigma = S_{st.} + bE$  also has the increasing property, where  $b$  is any universal constant. Now when we set out to define the absolute temperature scale, we must start with the general function  $\Sigma$  which has the increasing property, for we have as yet no right to choose any particular value for  $b$ . If we attempt to define  $T$  by the relation  $\partial \Sigma / \partial E = 1/T$ , we find

$$\frac{1}{T} = \frac{\partial \Sigma}{\partial E} = \frac{\partial S_{st.}}{\partial E} + b = k \log 1/\vartheta + b,$$

which can never determine absolutely the relation of  $T$  to  $\vartheta$  so long as  $b$  is undetermined.

This impasse is one aspect of the fact that in thermodynamics the absolute temperature and the entropy are introduced in the same chain of argument—the absolute temperature as integrating factor and the entropy as the resulting integral. Thus—and this is a point that has been overlooked by some writers—it is impossible to identify the entropy by using assemblies in which temperature is the only variable, for *any* function of the temperature is then a possible integrating factor. There is only one way of making the identification, and that is to evaluate  $dQ$ , the element of heat, for an assembly of more than one variable from our statistical principles, and to show that a certain unique\* function of the temperature  $\vartheta$  is an integrating factor for it. The use of functions with the increasing property can apparently never lead to precise results without this appeal to  $dQ$ . We shall therefore abandon the whole of the development of the preceding sections (4-7), including the Boltzmann Hypothesis, and shall establish from first principles that in fact the quantity  $dQ$  has a unique integrating factor depending only on  $\vartheta$ , and that this does lead to  $S_{st.}$  for the entropy.

### § 7. The Entropy from first principles.

By the definition of  $dQ$  †, we have

$$dQ = dE + \Sigma X dx, \quad . \quad . \quad . \quad . \quad (7.1)$$

where  $E$  is the energy of the assembly, the  $x$ 's are certain parameters defining the external fields, and the  $X$ 's the associated forces. Let us suppose a generalized assembly

\* Of course, an arbitrary constant multiplier excepted.

† The "heat"  $dQ$  taken in in any small change is defined in thermodynamics to be the increase in internal energy plus the external work done by the assembly. See *e. g.* Born, *loc. cit.*

composed of groups of systems; let there be  $M_r$  systems which have a partition function  $f_r$ . This means that if the possible conditions of one of these systems are that it should be able to have energies  $\epsilon_{r,1}, \epsilon_{r,2}, \dots$ , and associated with each of these states there is a weight factor  $p_{r,1}, p_{r,2}, \dots$ , then

$$f_r = \sum_t p_{r,t} \mathfrak{S}^{\epsilon_{r,t}},$$

or the limit of this expression if, as for mechanical as opposed to quantized systems, all the dimensions of the cells must tend to zero. In order to allow for changes of condition other than those of temperature, we must suppose that each  $\epsilon_{r,t}$  is a function of the parameters  $x_1, x_2, \dots$ ; for example, in the case of free molecules in a vessel the wall may be represented by a local field of strong repulsive force, and then the potential of this repulsive force must be contained in  $\epsilon_{r,t}$ . With these data we find at once by (2.3) that

$$E = \sum_r M_r \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log f_r, \quad \dots \quad (7.11)$$

and the average number of the  $r$ th group of systems in their  $t$ th cell is by (2.5)

$$\bar{a}_{r,t} = M_r p_{r,t} \mathfrak{S}^{\epsilon_{r,t}} / f_r(\mathfrak{S}, x_1, x_2, \dots). \quad \dots \quad (7.2)$$

We also require to evaluate the external work done by the assembly in any small displacement represented by small changes in the parameters. Now the potential energy due to the external bodies is contained in  $\epsilon_{r,t}$ , and it will give rise to reactions on the external bodies. If the positions of the bodies are defined by the parameters  $x_1, x_2, \dots$ , the reactions will be a set of generalized forces of amounts

$$-\frac{\partial}{\partial x_1} \epsilon_{r,t}, \quad -\frac{\partial}{\partial x_2} \epsilon_{r,t},$$

for each single system of group  $r$  in the  $t$ th cell. The total generalized force tending to alter the parameter  $x_1$  will thus be

$$\sum_{r,t} a_{r,t} \left( -\frac{\partial}{\partial x_1} \epsilon_{r,t} \right),$$

and its mean value will be

$$\begin{aligned} X_1 &= \sum_{r,t} \bar{a}_{r,t} \left( -\frac{\partial}{\partial x_1} \epsilon_{r,t} \right), \\ &= \sum_{r,t} M_r p_{r,t} \mathfrak{S}^{\epsilon_{r,t}} \left( -\frac{\partial}{\partial x_1} \epsilon_{r,t} \right) / f_r(\mathfrak{S}, x_1, x_2, \dots), \\ &= \frac{1}{\log 1/\mathfrak{S}} \frac{\partial}{\partial x_1} \sum_r M_r \log f_r(\mathfrak{S}, x_1, x_2, \dots). \quad \dots \quad (7.3) \end{aligned}$$



Then

$$\begin{aligned}
 dQ &= dE + X_1 dx_1 + X_2 dx_2 + \dots, \\
 &= \sum_r M_r \left\{ \left[ \frac{\partial}{\partial \mathfrak{S}} \log f_r + \mathfrak{S} \frac{\partial^2}{\partial \mathfrak{S}^2} \log f_r \right] d\mathfrak{S} \right. \\
 &\quad \left. + \left[ \mathfrak{S} \frac{\partial^2}{\partial \mathfrak{S} \partial x_1} \log f_r + \frac{1}{\log 1/\mathfrak{S}} \frac{\partial}{\partial x_1} \log f_r \right] dx_1 + \dots \right\}, \\
 &= \frac{1}{\log 1/\mathfrak{S}} \sum_r M_r d \left[ \log f_r + \log 1/\mathfrak{S} \cdot \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log f_r \right].
 \end{aligned}
 \tag{7.4}$$

It follows that  $\log (1/\mathfrak{S}) dQ$  is a perfect differential. We can therefore at once define the absolute temperature scale, so as to make  $dQ/T$  a perfect differential, by the equation

$$\log 1/\mathfrak{S} = 1/kT. \quad \dots \tag{7.5}$$

No function only of  $\mathfrak{S}$ , except  $\log 1/\mathfrak{S}$ , can be an integrating factor of  $dQ$ , and therefore the absolute temperature so defined is unique, apart from  $k$ , the constant undetermined factor which it always contains. Moreover, by definition of  $S_{th}$ ,  $dQ/T = dS_{th}$ , and therefore, except for one arbitrary additive constant,

$$\begin{aligned}
 S_{th} &= k \sum_r M_r \left( \log f_r + \log 1/\mathfrak{S} \cdot \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log f_r \right), \\
 &= S_{st}, \quad \dots \tag{7.6}
 \end{aligned}$$

where  $S_{st}$  is defined by (5.1). The identification of our statistical entropy with the entropy of thermodynamics is complete, and the rest of thermodynamics follows in due course, so long as the assemblies considered are of such types as to be representable by partition functions.

### § 8. The characteristic function of Planck.

We have presented the formal proof in its most familiar form, but we can now make the presentation mathematically much simpler. The expression (5.2) invites us to make our fundamental definition not that of entropy but of the "characteristic function" of Planck. This function  $\Psi$ , which is closely allied to the "free energy," is defined in thermodynamics by

$$\Psi = S - E/T. \quad \dots \tag{8.1}$$

The characteristic function has the properties

$$E = T^2 \frac{\partial \Psi}{\partial T}, \quad . \quad . \quad . \quad . \quad . \quad (8.2)$$

$$S = \Psi + T \frac{\partial \Psi}{\partial T}, \quad . \quad . \quad . \quad . \quad . \quad (8.21)$$

$$X_1 = T \frac{\partial \Psi}{\partial x_1}, \dots \quad . \quad . \quad . \quad . \quad . \quad (8.22)$$

DEFINITION.—*The characteristic function for any part of an assembly is  $k$  times the sum of the logarithms of the partition functions of all the component systems of the part when the argument of the partition functions is  $\mathfrak{S} = e^{-1/kT}$ .*

With this definition we can show at once that the thermodynamic processes are mathematically equivalent to those we have been carrying out from the statistical point of view. There is no need to repeat the work, as the mere change from  $T$  to  $\mathfrak{S}$  exactly transforms (8.2), (8.21), (8.22) into (7.11), (7.6), (7.3) if  $\Psi = k \sum_r M_r \log f_r(\mathfrak{S}, x_1, x_2, \dots)$ .

The characteristic function contains two arbitrary constants, which occur in the form  $S_0 - E_0/T$ . Of these,  $E_0$  is seen to correspond to the arbitrary zero of the energy of the systems, which appears in each exponent of the partition function. The constant  $S_0$  depends on the absolute values adopted for the weight factors. We have made the *convention* of taking this as unity for simple quantized systems; but it is only a convention, and quite without effect on the various average values, which are all that can ever be observed. Indeed, the only conditions attaching to the weight factors are *precisely* analogous to those attaching to entropy in classical thermodynamics—a definite ratio is required between the weights of states of systems which can pass from one to the other (as in the dissociation of molecules);—but as long as two systems are mutually not convertible into one another, it makes absolutely no difference what choice is made for their relative weights.

Many writers have attempted to give reality to the convention that weight has an absolute value, and from it have defined *absolute entropy*. Such a definition cannot possibly make any difference in any thermodynamic results; but the object was mainly to deal with the Nernst Heat Theorem, and there it has been successful. It is, however, much more rational to do without this somewhat mystical idea, and to suppose that the theorem is a consequence of the equality of weights of any allotropic forms in the states of lowest energy

that they may possess. The abandonment of absolute entropy involves of course the acceptance of the paradox that the entropy of 2 grammes of gas may not be twice that of 1 gramme; but this paradox causes no real difficulty\*.

§ 9. *The "canonical ensemble" of Gibbs, and its relation to a temperature bath.*

It is important to consider also the general question of the truth of the Second Law as deduced statistically for assemblies which are of some more complex type for which the energy cannot be separated up in the way that has hitherto been possible: any general proof must cover such cases. Now Gibbs' work deals with these generalized assemblies, and he establishes with great simplicity the necessary theorems, provided that he may start by postulating the conditions of the "canonical ensemble." But the idea of "canonical" is not very easily defined, and it leaves a slight feeling that there might be somewhere in it a *petitio principii*. He later turns over to the "micro-canonical" conditions, but the calculus becomes rather heavy. With our present method we can very quickly show that Gibbs' "canonical ensemble of phases" is, for the purpose of averaging, equivalent to having our assembly of systems in a temperature bath.

Consider an assembly composed of a mechanical system of  $n$  degrees of freedom, with coordinates  $Q_1 \dots Q_n$  and momenta  $P_1 \dots P_n$ , together with a very large number  $M$  of systems of any of the types we have treated. The mechanical system exchanges energy with the others, but for the greater part of its motion we may, as usual, think of it undisturbed and in possession of a definite energy of its own. For simplicity we may suppose the temperature to be the only variable in the partition function  $j$  of the systems of the bath, though this is quite immaterial. Let the various weight factors be  $p_0, p_1, \dots$  and energies  $\epsilon_0, \epsilon_1, \dots$  so that the partition function is  $j(\mathcal{S}) = \sum_r p_r \mathcal{S}^{\epsilon_r}$ . For the mechanical system we must take any element of phase  $d\Omega (= dQ_1 \dots dP_n)$  as having weight  $d\Omega/h^n$ , by the principles described in § 2 of our former paper.

Now consider arrangements in which the mechanical system is in  $d\Omega$ , while for the bath there are  $a_0, a_1, a_2, \dots$  systems respectively in states 0, 1, 2, .... By the methods

\* Ehrenfest and Trkal, *loc. cit.*

of our former paper the number of weighted complexions will be

$$\frac{M!}{a_0! a_1! \dots} p_0^{a_0} p_1^{a_1} \dots \frac{d\Omega}{h^n}, \quad . \quad . \quad . \quad (9.1)$$

and we must have

$$\Sigma_r a_r = M, \quad \Sigma_r a_r \epsilon_r + \epsilon = E. \quad . \quad . \quad . \quad (9.2)$$

The probability that the mechanical system is in  $d\Omega$  is measured by the total number of complexions for which it is there, and so (9.1) must be summed over all values of the  $a$ 's consistent with (9.2). Now if  $\mathfrak{S}$  is the solution of

$$E - \epsilon = M\mathfrak{S} \frac{d}{d\mathfrak{S}} \log f, \quad . \quad . \quad . \quad (9.3)$$

this sum is

$$\frac{[f(\mathfrak{S})]^{M\mathfrak{S}\epsilon}}{\mathfrak{S}^E \left\{ 2\pi M \left( \mathfrak{S} \frac{d}{d\mathfrak{S}} \right)^2 \log f \right\}^{\frac{1}{2}}} \frac{d\Omega}{h^n},$$

by virtue of § 6 of our former paper. Here  $\mathfrak{S}$  is, strictly speaking, the exact temperature of the bath at the moment under consideration, and so will be liable to fluctuation according to the value of  $\epsilon$ ; but, by virtue of the assumption that the bath is very large,  $\epsilon$  will practically always be insignificant in the solution of (9.3), and so  $\mathfrak{S}$  may be taken as a constant. Then the probability that the mechanical system is in the cell  $d\Omega$  is proportional to  $\mathfrak{S}^\epsilon d\Omega$ , and all the other factors are constant and may be omitted in taking averages. Using (7.5) we thus obtain Gibbs' expression for the density-in-phase of the "canonical ensemble," namely

$$e^{-\epsilon/kT} dQ_1 \dots dP_n.$$

This leads to the impossibility of perpetual motion and all his work on the laws of thermodynamics.

#### § 10. *The Deduction of the Elementary States from Thermodynamic Data.*

An interesting result follows from the inversion of the argument of § 8. Suppose that we have an assembly of unknown constitution in which the temperature is sole variable. Then a knowledge of the specific heat determines the characteristic function, and thence the partition function. If this can be expanded in terms of  $\mathfrak{S}$ , we can determine the energies and weights of the elementary states; but the matter is complicated by the fact that we cannot tell in



advance the size of the units of energy in which the expansion is to be made.

The problem is exactly analogous to that solved by Poincaré\* in his deduction of the necessity for quanta from the fact that Planck's radiation formula agrees with experiment. The machinery required has been examined by one † of us in a recent paper. We give here a sketch of how it may be applied to the present problem: reference must be made to the original works for further detail. If we write  $\tau = 1/kT$ , we may suppose that the partition function is known in terms of  $\tau$ . The relation of the partition function to the weights and energies from which it is generated may be put in the form of a Stieltjes' integral:—

$$f(\tau) = \int_0^{\infty} e^{-\tau\epsilon} dw(\epsilon).$$

Here  $dw(\epsilon)$  represents the weight corresponding to  $\epsilon$ , and it is indifferent whether we are concerned with quantized systems or mechanical ones with continuous distributions of weight. The function  $w(\epsilon)$  can be determined by an extension of the method of the Fourier integrals, which (roughly speaking) leads to

$$w(\epsilon) = \frac{1}{2\pi i} \int_{\alpha-i\infty}^{\alpha+i\infty} f(\tau) e^{\epsilon\tau} \frac{d\tau}{\tau},$$

where  $\alpha$  can have any positive value above a certain limit.

This is a complete solution, but it requires that  $f$  should be known for complex values of  $\tau$ , and in practice it would be given in the form of a table, of course for real  $\tau$  only. In general it would not be possible to find a simple analytic expression to fit with the tabular values. This difficulty can, however, be turned ‡, so that only the practical difficulty of carrying out a large number of mechanical quadratures would remain. For it is possible to associate with the real function  $f(\tau)$  a complex function

$$J(q) = \int_0^{\infty} f(\tau) \tau^{q-1} d\tau,$$

where  $q$  may have complex values, and then

$$w(\epsilon) = \frac{1}{2\pi i} \int_{\alpha-i\infty}^{\alpha+i\infty} \frac{J(q)}{\Gamma(q)} \epsilon^q \frac{dq}{q}.$$

This is the formal solution of the problem; but it must be doubtful whether it is really a practical method.

\* Poincaré, *Journal de Physique*, ser. v. vol. ii. p. 5 (1912).

† Fowler, *Proc. Roy. Soc. A.* vol. xcix. p. 462 (1921).

‡ Fowler, *loc. cit.* § 5.

In this paper and its predecessor we have discussed the relation of statistical theory to thermodynamics in detail only for a rather limited class of systems, though it is practically the class in which alone success has been attained by anyone. It is at least doubtful how much further the combinatory calculus can be pushed; as soon as the multinomial theorem ceases to apply (as it would for imperfect gases) great difficulties are encountered in our method, but these difficulties are largely inherent in such problems. In spite of these limitations, it would appear that the potentialities of the method are by no means exhausted.

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LXXII. *The normal Helium Atom and its relation to the Quantum Theory.* By J. H. VAN VLECK, *Jefferson Physical Laboratory, Harvard University, Cambridge, Mass. (U.S.A.).\**

PART I. of this paper is of a non-mathematical character, and is concerned with the difficulties associated with finding a satisfactory quantum theory model of normal helium. After a *résumé* of existing models, a study is made of the model suggested by Dr. E. C. Kemble in which the two electrons are arranged with axial symmetry, the one symmetrical type whose energy has not yet been computed. As the result of a rather laborious calculation, a value is obtained for the ionization potential of this model which is not in agreement with experiment, the discrepancy being slightly greater than for the Bohr model.

Because of the failure of this model with axial symmetry, it does not seem possible to devise a satisfactory symmetrical model of helium based on the conventional quantum theory of atomic structure, and the remainder of Part I. therefore deals with the modifications in the ordinary conception of the quantum theory or of the electron which may be necessary in order to escape from this dilemma. Two suggestions on reformulation of the quantum conditions made by Langmuir are criticized, and a frankly empirical rule for determining the stationary states is suggested which leads to approximately the correct energy values for the helium atom, the hydrogen molecule, and the positively charged

\* Communicated by Prof. Lyman.

hydrogen ion. The difficulties confronting modification of the law of force between negative electrons as an alternative method of explaining the dilemma of the helium atom are also discussed.

Part II. assumes no knowledge of the quantum theory and is an outline of the mathematical method used in finding the orbits in the model of helium in which the two electrons are arranged with axial symmetry. This method consists in developing the perturbations as power series in a constant of integration, and is readily adaptable to other problems in the dynamics of atomic structure. A simple check on the accuracy of solution is furnished by the theorem that the average absolute values of the kinetic energy and half the potential energy are equal.

Part III. deals with applications of quantum conditions to the determination of the energy for the model of helium possessing axial symmetry. Various theories for determining the stationary states prove to lead consistently to the same values for the constants of integration.

The writer wishes to express his gratitude for the encouragement and assistance given him by Dr. E. C. Kemble in the problems studied.

## PART I.—THE DILEMMA OF THE HELIUM ATOM.

### *Résumé of Existing Models of normal Helium.*

Probably the greatest success the quantum theory has yet achieved is found in the Bohr atom, in which the electron is allowed to move only in certain quantized non-radiating orbits. However, the quantitative success of the Bohr theory in explaining spectral lines and ionization potentials has been confined to atoms containing only a single electron, viz., the hydrogen atom and an abnormal helium atom which has been robbed by ionization of one of its two electrons normally present. In generalizing the theory to apply to atoms with more than one electron, it is natural to begin with the simplest possible case, namely, the normal helium atom, which contains only two electrons.

Numerous attempts have been made to construct quantum theory models of normal helium. In Bohr's own model (fig. 1) the two electrons revolve about the nucleus at the extremities of a diameter\*. In the Langmuir semicircular

\* Phil. Mag. vol. xxvi. p. 492 (1913).

model (fig. 2) the two electrons describe an oscillatory motion in a plane, always being symmetrically situated with respect to an axis passing through the nucleus\*. In the Landé† and the Franck and Reiche‡ models the electrons have more complicated orbits of unequal size, which are coplanar only in the case of the Landé model (fig. 3). In the Langmuir double-circle model (fig. 4) the orbits are circles lying in two parallel planes\*.

Fig. 1.

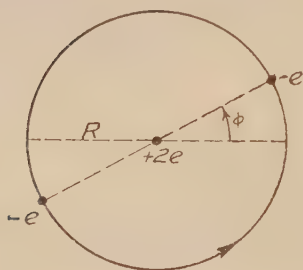


Fig. 2.

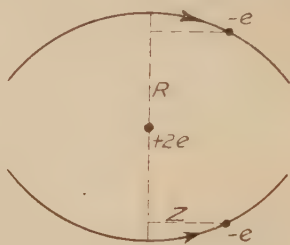


Fig. 3.

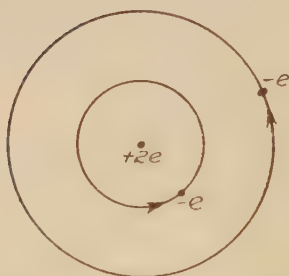
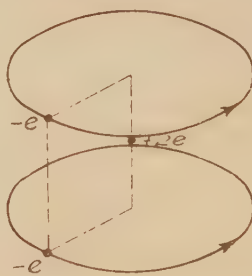


Fig. 4.



The dimensions of these models must be determined by applying the Sommerfeld-Wilson quantum conditions, which state that

$$\oint p dq = nh,$$

where  $h$  is Planck's constant,  $n$  is an integer,  $q$  is an appropriately chosen generalized coordinate, and  $p$  is its conjugate momentum  $\frac{\partial T}{\partial \dot{q}}$ . The integration is to be extended over a

\* Physical Review, vol. xvii. p. 339 (Mar. 1921).

† Phys. Zeits. xx. p. 233 (1919) and xxi. p. 114 (1920).

‡ Zeits. f. Phys. i. 2, p. 154 (1920); Phil. Mag. vol. xlii. p. 125.



complete cycle of values of  $q$ . Having thus determined the dimensions, we can compute the energy and compare the calculated value with that found experimentally from ionization potentials. In no case is the agreement satisfactory, so that apparently none of these models can be correct if the Sommerfeld quantum conditions are accepted. For a more thorough exposition of the difficulties confronting these models the reader is referred to a recent paper by E. C. Kemble in the *Philosophical Magazine* \*.

Since none of these models can be regarded as thoroughly satisfactory, it is natural to inquire whether there cannot be some other possible model. In making this investigation we must bear in mind that the extreme chemical stability of helium indicates that the arrangement of its two electrons is particularly simple and symmetrical, for an electron revolving in an orbit outside that of its mate would presumably be a valence electron. Symmetry with respect to a point yields the Bohr model, already mentioned. The two simplest cases of symmetry with respect to a plane (figs. 2 and 4) have been investigated by Langmuir, and yield impossible ionization potentials of approximately the same size ( $-4.6$  and  $-8.5$  volts) †. It is extremely doubtful whether other more complicated, and therefore less probable, orbits symmetric with respect to a plane would yield ionization potentials differing very widely from those of these two simple limiting cases ‡.

### *Study of Model with Axial Symmetry.*

The only remaining type of simple symmetry which has not been studied is that with respect to an axis. It therefore seemed desirable to compute the ionization potential of a model possessing this kind of symmetry, which was suggested by Dr. E. C. Kemble §. Since the two electrons I. and II. move in three dimensions so as to always be symmetrically located with respect to an axis,

\* *Phil. Mag.* vol. xlii. p. 123 (July 1921).

† *Physical Review*, vol. xvii. p. 339.

‡ *Cf.* identity of elliptical and circular energy levels in the hydrogen atom (relativity corrections neglected). In the two Langmuir models, projection of motion on plane of symmetry is a straight line or circle. The most general motion symmetric with respect to a plane would project into a sort of precessing ellipse, which may be regarded as intermediate between the above two cases. The more general motion might involve impossible singularities, such as continual distortion of shape of ellipse.

§ *Loc. cit.*

their cylindrical coordinates are

$$\text{I. } R, Z, \phi, \quad \text{II. } R, Z, \phi + \pi,$$

the  $Z$  axis being that of symmetry. This model may be regarded as a sort of hybrid of the Bohr and Langmuir models. The constant angular momentum, which the electrons possess about the axis of symmetry, reminds one of the Bohr model, and the projection of the motion on the plane  $Z=0$ , which is normal to the axis of symmetry, is a sort of precessing ellipse. The type of motion in the  $RZ$  plane can be seen by returning to fig. 2. This motion is of an oscillatory character, and is similar to that of the Langmuir semicircular model, except for the effect of a centrifugal force term introduced by the rotation of the  $RZ$  plane about the axis of symmetry as the coordinate  $\phi$  steadily increases. The motion may be approximately described as the projection of a sine curve on a barrel-shaped surface of revolution, the two electrons always being on opposite sides of the barrel.

Rough preliminary calculations for this model indicated approximate agreement of the computed and observed ionization potentials, and it was therefore necessary to carry through a more accurate solution of the dynamical problem, which took almost six months. The orbits of the electrons in the helium atom were determined as power series in a constant of integration, a mathematical method often used by astronomers in the three body problems of the solar system. A more detailed description of the mathematics used in solving the dynamical problem, as well as the method used to check the accuracy of solution, is given in Part II.

After solution of the dynamical problem, the constants of integration were determined by the quantum conditions (see Part III.), and the ionization potential was then computed, which proved to be 20.7 volts for the removal of one electron or 74.9 volts for the removal of both electrons. This does not agree with the experimental value of  $25.4 \pm .25$  volts\*, but the discrepancy is only slightly larger than for the Bohr model, which yields 28.8 volts, the closest agreement obtained by any model based purely on the Sommerfeld quantum conditions.

#### *The Dilemma of the Helium Atom.*

As already mentioned, the extraordinary chemical stability of helium indicates that the arrangement of its pair of electrons is particularly simple and symmetrical, but all

\* Frauck and Knipping, *Phys. Zeit.* xx. p. 481 (1919).

models possessing this property now appear to have been weighed in the balance and found wanting, as they lead to impossible energy values. The conventional quantum theory of atomic structure does not appear able to account for the properties of even such a simple element as helium, and to escape from this dilemma some radical modification in the ordinary conceptions of the quantum theory or of the electron may be necessary\*. One such possibility is :

### *Reformulation of the Quantum Conditions.*

Any reformulation of the quantum conditions which aims to explain the anomaly of the helium atom by permitting new energy values must yield results identical with those of the ordinary Sommerfeld quantum integrals in the cases of the hydrogen atom and a vibrating diatomic molecule, for in these instances the Sommerfeld conditions are verified by a mass of experimental evidence.

Two very interesting suggestions on reformulation of the quantum conditions have been made by Langmuir †. One of these suggestions is that in a system with two negative electrons the ordinary Sommerfeld integrals should be replaced by the condition that the maximum angular momentum of a single electron be set equal to  $\frac{h}{2\pi}$ . In Langmuir's semicircular helium atom (fig. 2), this maximum value  $\frac{h}{2\pi}$  would be achieved when each electron is at the middle of its path, so that we may regard the atom as having two quantum units of angular momentum circulating about the nucleus in opposite directions. This new condition for determining the constants of integration yields the correct ionization potential for the semicircular model of helium ‡, and therefore merits serious consideration. However, it appears to be a contradiction, rather than generalization, of the Sommerfeld quantum conditions, for in the

\* The possibility of some asymmetrical model of normal helium should perhaps not be entirely rejected, despite its apparent contradiction to the view of chemists on the symmetry of helium. In this connexion it should be mentioned that the energies of the Landé and the Franck and Reiche models are not computed directly, but are obtained by extrapolation of spectral series terms. This extrapolation pre-supposes the validity of the Landé theory of the helium spectrum. Also the continuation of a curve can never be predicted with absolute certainty by extrapolation.

† Physical Review, vol. xvii. p. 339, vol. xviii. p. 104 (1921); also Science, vol. lli. p. 434.

hydrogen atom and the diatomic molecules of band spectrum theory it is the total angular momentum of the entire system (comprising two bodies), rather than the maximum angular momentum of a single electron, which must be equal to

$\frac{h}{2\pi}$ . Also one would expect Langmuir's new quantum

condition to be equally applicable to his semicircular model of the hydrogen molecule, for the latter is almost identical with his semicircular helium atom, as the two electrons oscillate back and forth about the centre of the line joining the two hydrogen nuclei. However, computations made by the writer indicate that the maximum angular momentum of

a single electron must be  $0.55 \frac{h}{2\pi}$ , instead of exactly  $\frac{h}{2\pi}$ , if the

ionization potential of hydrogen is to have the proper value, so that the scheme which works so well in helium does not seem to yield correct results for a similar case in hydrogen.

Langmuir's other suggestion consists essentially in replacing the centrifugal force term found in the ordinary dynamical Bohr theory of the hydrogen atom by a statical force of equal magnitude, leading to a static atom. This force may be accounted for by assuming that the electron is

an electrical doublet of strength  $\frac{1}{2em} \left( \frac{nh}{2\pi} \right)^2$ . The super-

position of this new static force on the ordinary Coulomb force appears contradictory to the scattering experiments of Rutherford on the validity of the inverse square law, and to the dynamical orbits found in band spectrum and specific heat theory. This static theory yields the correct ionization potentials for the helium atom and the hydrogen molecule\*, but the strength of the electrical doublet would have to be modified to depend on the mass of the attracting nucleus, which is highly improbable, in order to explain the observed shift between the lines of the Balmer series of hydrogen and those of the Pickering series of helium, a shift which the ordinary dynamical theory naturally accounts for as a correction for the motion of the nucleus. A further objection to the electrical doublet interpretation of the new static force is that the doublet would presumably orient itself so as to be attracted rather than repelled by the nucleus, giving a force of wrong sign (centripetal rather than centrifugal). Other difficulties confronting any static atom are explanation of the Stark and

\* Bulletin of the National Research Council, no. 14, p. 347.



Zeeman effects, the selection principle, and the Sommerfeld fine-structure.

In periodic motions the so-called action integral is

$$2 \int_0^{\tau} T dt,$$

where  $T$  is the kinetic energy and  $\tau$  is the period of the motion. In view of the fact that in periodic motion this quantity is an adiabatic invariant, and that according to the relativity principle its value is independent of the particular set of Galilean axes chosen as a reference system, one might expect any form of quantum conditions to be expressible in the form of a restriction on the value of the action integral. If the ionization potential of the Langmuir semicircular helium atom is to have the proper value, its action integral must be equal to  $1.578 h$ , while the corresponding value for the semicircular hydrogen molecule is  $1.399 h$  \*. A very good approximation to these values is obtained by assuming that the action integral associated with one electron can have the

value  $\left(\frac{\pi}{4}\right)^{\frac{m}{2}} h$ , where  $m$  is an integer.  $m$  must be taken equal to zero for the hydrogen atom and the K ring of X-rays, while we shall set  $m=2$  for the normal helium atom and the positively-charged hydrogen ion (systems with three bodies) and  $m=3$  for the hydrogen molecule (a system with four bodies). This yields  $1.571 h$  for the action integral of the helium atom and  $1.393 h$  in the case of the hydrogen molecule. Also for a model of the positively charged hydrogen ion in which the electron revolves about the centre of the line joining the two nuclei †, this rule gives an ionization potential of 11.48 volts, which agrees well with the experimental value of  $11.5 \pm .7$  volts found by Franck, Knipping, and Krüger ‡. In the cases of the helium atom and the hydrogen molecule, the agreement is not quite as good as might be desired, but it does not appear impossible to explain the discrepancy as due to experimental errors in measurement of the ionization potential and in determination of the atomic constants  $e, h, m$ .

\* These quantities are readily computed from data in Langmuir's papers (Science, vol. lli. p. 434; Physical Review, vol. xvii. p. 352). Computation for helium has also been made by E. C. Kemble (Science, vol. lli. p. 581). In calculations, ionization potentials of helium and hydrogen atoms were taken as 25.4 and 13.55 volts, and heat of dissociation of hydrogen as 84,000 calories/mol.

† Cf. Sommerfeld, 'Atombau und Spektrallinien,' 2nd ed. p. 514.

‡ Verh. d. D. Phys. Ges. xxi. p. 728 (1919).

The writer has not been able to find any theoretical basis for these empirical rules, and they appear rather hard to reconcile with the Bohr Analogy Principle, but it should be remembered that the type of dynamical system to which they are applied is somewhat different from that met with in the hydrogen atom, where (with neglect of relativity correction) the action integral can only be an integral multiple of  $h^*$ . Also the atomic models to which these empirical rules appear applicable are those whose physical properties seem to be in best agreement with experiment. This is especially true as regards the semicircular model of the hydrogen molecule, while the case of the helium atom will be discussed on later pages. The moment of inertia of the semicircular model of the hydrogen molecule agrees well with the value found from band spectra, while its zero angular momentum about the axis of symmetry is in accordance with specific heat theory, the diamagnetism of hydrogen, and the behaviour of the many-lined hydrogen spectrum in a magnetic field†. No other model has been proposed which possesses these properties.

*Modification of Law of Force between Negative Electrons.*

In the absence of any thoroughly satisfactory attempt at reformulating the quantum conditions, we must consider as an alternative the modification of the law of force between negative electrons at atomic distances. Any alteration of the law of force between negative electrons and positive nuclei (such, for instance, as would result from a highly aspherical nucleus) would probably invalidate the Bohr theory of the hydrogen atom and contradict the experimental evidence of Rutherford on the validity of the inverse square law, but his work yields no information on the forces between two negative electrons‡. On the other hand, A. H. Compton concludes that the spiral tracks of beta particles indicate that the field of an electron does not have the

\* Cf. remark by Bohr: "Diese Störungen (*i. e.*, mutual action between electrons) geben nämlich für die beiden Partikeln des Heliumatoms zur Bewegungen Anlass, deren Charakter sich als überaus verwickelt erweist, und zwar so, dass die stationären Zustände nicht festgesetzt werden können in direkter Anlehnung an die Methoden die für bedingt periodische Systeme entwickelt worden sind" (*Zeits. für Physik*, Band 2, Heft 5, p. 465).

† Cf. Langmuir, *Science*, vol. lli. p. 434, *Physical Review*, vol. xvii. p. 339.

‡ In a very recent paper (*Proc. Roy. Soc.*, Feb. 1922), Crowther and Schonland, however, conclude that some modification of law of force at *very small* distances, either between two negative electrons or an electron and a nucleus, appears to be demanded by their experiments on the scattering of beta particles.

spherical symmetry demanded by the Coulomb law \*. One way to account for the magnitude of the observed dissymmetry is to assume that the electron is a magnetic doublet of strength about  $10^{-20}$  E.M.U. \* (such as would be produced by a rotating ring of electricity having one quantum unit  $\frac{h}{2\pi}$  of angular momentum). However, the strength of the magnetic doublet would have to be about  $5 \times 10^{-19}$  E.M.U., a value fifty times as large as that given above, in order to have the desired effect on the ionization potential of helium. The existence of a magnetic doublet of such a large size could not be reconciled with observed molecular magnetic moments, which are very much smaller, and would invalidate the classical theory of the scattering of X-rays, as the magnetic forces acting on this magnetic electron would be comparable with the electrical forces when the wave-length of the impressed beam of light did not exceed the atomic diameter. It is doubtful whether it is possible to attribute to an electrical or magnetic origin departures from the inverse square law of sufficient magnitude to explain the anomalies of normal helium. Instead it would be necessary to introduce a "mystery force," which is negligible except at atomic distances, and which does not have a mechanism based on the Maxwell field-equations. This new force should explain the spiral tracks of beta particles as well as the properties of helium. In support of the idea of introducing this rather arbitrary "mystery force," it should be stated that it is not improbable that such a bold hypothesis may be necessary in order to explain the stability of atomic nuclei. A cogent argument against modification of the law of force between negative electrons is that it cannot account for the absence of a satisfactory model of the positively charged hydrogen ion, which contains only one electron. Also a simple computation shows that a mystery force between electrons depending only on their relative distance (consequently developable in a series in inverse powers of the distance) would invalidate the Sommerfeld-Kossel theory of X-rays †.

\* A. H. Compton, *Phil. Mag.* vol. xli. p. 279, Feb. 1921.

† This follows as a consequence of the fact that centrifugal force  $mR\dot{\phi}^2 = \frac{\hbar^2}{4\pi^2 m R}$  acting on an electron having one quantum unit  $\frac{h}{2\pi}$  of angular momentum varies inversely as the cube of the radius as the latter changes from element to element in the K ring. Therefore an inverse cube mystery force comparable with the centrifugal force in the helium atom, so as to give the required alteration in the ionization potential, would also be comparable with the centrifugal force in the K rings of elements of higher atomic number, and hence would have an appreciable effect on the energy. With mystery forces involving higher inverse powers, the effect would be even larger.

and to retain the latter it would appear necessary to make some artificial and improbable assumption concerning the character of the mystery force, such as having it depend on the velocity in such a way that it became negligible at the high velocities found in the electrons of the K and L rings.

### Conclusion.

As yet it appears possible to devise a satisfactory symmetrical model of the normal helium atom only with the aid of some such radical innovation as reformulation of the quantum conditions or modification of the law of force between negative electrons. The probability of the latter alternative is discounted by the success of the ordinary quantum theory of X-rays. It is to be hoped that with *one* such bold hypothesis we can *simultaneously* obtain the proper energy values for models both of the helium atom and the hydrogen molecule. The models of normal helium which are physically most plausible seem to be the Langmuir semicircular one or that with axial symmetry. The zero resultant angular momentum of the Langmuir model is perhaps in best accord with the observed diamagnetism of helium, and if the semicircular model of the hydrogen model is correct, one would expect the normal helium atom to be of a similar type. However, the type with axial symmetry has the advantage of requiring smaller departures from the conventional quantum conditions or less readjustment of the law of force in order to obtain the correct ionization potential\*. Some very interesting experimental evidence on the structure of the helium atom is given in a recent article by Millikan†. Observations taken with his oil-drop apparatus indicate that when an alpha particle collides with a helium atom it hurls out both electrons about 16 per cent. of the time, while during the remaining 84 per cent. of the collisions it ejects only one electron. This, Millikan concludes, eliminates the possibility of the Bohr model of normal helium, as the chances of the incident alpha particle having just the right direction to collide with the second electron after already striking the first one would be exceedingly small in a model of this character. Models such as those of Landé or Franck and Reiche, in which the two electron orbits differ considerably in size, are also rejected, as the innermost orbit exposes

\* The modifications would have to produce a change of 30.0 volts in the ionization potential for the semicircular model as compared with 4.7 volts for the type with axial symmetry.

† Physical Review, vol. xviii. p. 456, Dec. 1921.



too small an area for possible collisions. Instead, Millikan concludes that the correct model is one in which the orbits are of equal size and inclined at an angle of  $60^\circ$  or  $90^\circ$ , so that the two electrons might be in the same part of the atomic volume about one-sixth of the time. The type in which the two orbits are oriented at  $90^\circ$  does not appear to be allowed by the quantum conditions, while that in which the inclination is approximately  $60^\circ$  is that studied in detail in the present article. However, it appears to the writer that in addition to this model with axial symmetry the Langmuir semi-circular model is also in accord with the experimental evidence, although Millikan does not mention this possibility, for an incident alpha particle would probably eject both electrons when they are close together at the extremities of their paths (see fig. 2).

## PART II.—SOLUTION OF DYNAMICAL PROBLEM OF MODEL OF HELIUM IN WHICH ELECTRONS ARE ARRANGED WITH AXIAL SYMMETRY.

### *Introduction.*

Besides its direct bearing on the study of the helium atom, the determination of the orbits in a model of helium in which the electrons are arranged with axial symmetry is of interest as a solution of a special case of the problem of three bodies, and as an illustration of how the standard methods of celestial mechanics may be employed to solve the dynamical problem of sub-atomic physics. As no set of coordinates was found which would separate the variables in the Hamilton-Jacobi partial differential equation and thus yield an exact solution in closed form, it was necessary to have recourse to methods of perturbations, similar to those used by astronomers in lunar theory, etc. The method of celestial mechanics which is particularly applicable to our problem is that in which the perturbations are developed as power series in a parameter\*. The particular parameter selected was a constant of integration depending on the inclination of the two electron orbits relative to each other.

\* The other standard astronomical method, one based on successive approximations and mechanical integrations, cannot readily be employed, because the constants of integration are not known in advance but must be determined by quantum conditions after the solution is obtained. This other method, however, could be and was used by Langmuir in his semicircular helium atom, as the only arbitrary constants were scale of model and origin of time, while two additional constants appear in the present problem.

The solution is thus obtained in the form of a family of orbits, each member of which corresponds to a particular numerical value of the constant of integration in which the power series development was performed, and hence to a particular angle between the plane of the two electron orbits.

*Derivation of Equations of Motion.*

If the  $Z$  axis be taken as that of symmetry, the cylindrical coordinates of the two electrons I. and II. are

$$\text{I. } R, Z, \phi, \quad \text{II. } R, Z, \phi + \pi \quad (\text{cf. figs. 1 and 2}).$$

Because of the very large mass of the nucleus, its motion may be neglected, so that the total kinetic energy of the system is that due to the two electrons, viz.:

$$T = m[\dot{R}^2 + R^2\dot{\phi}^2 + \dot{Z}^2], \quad \dots \dots (1)$$

while the potential energy is

$$V = \frac{-4e^2}{\sqrt{R^2 + Z^2}} + \frac{e^2}{2R}, \quad \dots \dots (2)$$

where  $m$  is the mass and  $-e$  is the charge of an electron. The term  $\frac{e^2}{2R}$  represents the mutual potential energy of the electrons, while the term

$$\frac{-4e^2}{\sqrt{R^2 + Z^2}}$$

corresponds to the attraction exerted on the two electrons by the positive nucleus, whose charge is  $+2e$ . The Lagrangian equation

$$\frac{d}{dt} \left( \frac{\partial T}{\partial \dot{\phi}} \right) - \frac{\partial T}{\partial \phi} = - \frac{\partial V}{\partial \phi}$$

gives us immediately the first integral

$$2mR^2\dot{\phi} = p, \quad \dots \dots (3)$$

where  $p$  is a constant equal to the resultant angular momentum of the system. The corresponding Lagrangian

equations for R and Z are

$$m\ddot{R} - mR\dot{\phi}^2 = \frac{e^2}{4R} - \frac{2e^2R}{(R^2 + Z^2)^{3/2}}, \quad \dots \quad (4)$$

$$m\ddot{Z} = \frac{-2e^2Z}{(R^2 + Z^2)^{3/2}}. \quad \dots \quad (5)$$

If we eliminate  $\dot{\phi}$  by means of the relation (3), equation (4) becomes

$$m\ddot{R} = \frac{p^2}{4mR^3} + \frac{1}{4} \frac{e^2}{R^2} - \frac{2e^2R}{(R^2 + Z^2)^{3/2}}. \quad \dots \quad (6)$$

It will be found convenient to use certain reduced units expressing the fact that the scale of the model is arbitrary. Let

$$B^2 = \frac{2e^2}{mA^3}, \quad r = \frac{R}{A}, \quad \zeta = \frac{Z}{A}, \quad C = \frac{p^2}{8me^2A}, \quad \dots \quad (7)$$

where A is a constant depending on the size of the model. The equations of motion then take the form

$$\frac{r^3 \ddot{r}}{B^2} = C + \frac{1}{8}r - \frac{r^4}{(r^2 + \zeta^2)^{3/2}}, \quad \dots \quad (8)$$

$$\frac{\ddot{\zeta}}{B^2} = - \frac{\zeta}{(r^2 + \zeta^2)^{3/2}}. \quad \dots \quad (9)$$

### *Development of Solution as Perturbations from Circular Orbits.*

Let

$$\eta = \sqrt{1 - w \cos^2 Bt}, \quad S = w^{\frac{1}{2}} \cos Bt,$$

where  $w$  is a positive constant less than unity. If we neglect the term  $\frac{1}{8}r$  in equation (8), which is due to the force of repulsion between the negative electrons,  $r = \eta$ ,  $\zeta = S$  will be an exact solution of the dynamical problem provided the constants  $p$ ,  $A$ , and  $w$  satisfy the relation  $C = 1 - w$ . The two electrons then revolve about the nucleus in the familiar circular orbits found in the problem of two bodies. The intersection of the planes of the two orbits is a nodal line perpendicular to the axis of symmetry.  $w^{\frac{1}{2}}$  is the sine of the angle between the plane of one of the orbits and the plane normal to the axis of symmetry.

To obtain a solution of the complete equations of motion let us write

$$r = \eta + \rho, \quad \zeta = S + s$$

$\rho$  and  $s$  are then the perturbations from the circular motion caused by the forces of repulsion between the two electrons. Since  $\rho$  and  $s$  are small compared with  $\eta$ , we can expand the various terms in equations (8) and (9) as power series in  $\rho$  and  $s$ , and with sufficient accuracy for our purposes neglect terms of third or higher degree in  $\rho$  and  $s$ . When these expansions are performed, (8) and (9) become

$$\begin{aligned} \frac{\ddot{\rho}\eta^3}{B^2} + \rho \left[ \frac{3(1-w)}{\eta} - \frac{1}{8} + \eta^3 - 3\eta^5 \right] \\ = \left\{ C - 1 + w + \frac{1}{8}\eta + 3s\eta^4S + \rho^2 \left[ \frac{-3(1-w)}{\eta^2} - 3\eta^2 + \frac{27}{2}\eta^4 \right. \right. \\ \left. \left. - \frac{15}{2}\eta^6 \right] - \frac{3\ddot{\rho}\rho\eta^2}{B^2} + \rho s \left[ 12\eta^3S - 15\eta^5S \right] \right. \\ \left. + s^2 \left[ \frac{3}{2}\eta^4 - \frac{15}{2}\eta^4S^2 \right] \right\}, \quad \dots \dots \dots (10) \end{aligned}$$

$$\begin{aligned} \frac{\ddot{s}}{B^2} + s = 3\rho S\eta + 3sS^2 + \rho^2 \left[ \frac{3}{2}S - \frac{15}{2}\eta^2S \right] \\ + \rho s \left[ 3\eta - 15\eta S^2 \right] + s^2 \left[ \frac{9}{2}S - \frac{15}{2}S^3 \right] \dots \dots \dots (11) \end{aligned}$$

In obtaining these equations simplifications have been effected by combining coefficients of like powers of  $\rho$  and  $s$ , and by using the identities

$$\eta^2 + S^2 = 1, \quad \frac{\dot{\eta}\eta^3}{B^2} + \eta^4 = 1 - w, \quad \frac{\dot{S}}{B^2} = -S.$$

#### *Development of Perturbations as Power Series in the Constant w.*

The differential equations of motion are perhaps most readily solved by developing  $\rho$  and  $s$  as power series in the constant of integration  $w$ . With this method the solution can be built up step by step by equating to zero coefficients of successive powers of  $w$  in equations (10) and (11). The equations obtained by equating these coefficients to zero are linear and prove to be readily integrable. In order to obtain this series development it is first necessary to expand the various powers of  $\eta = \sqrt{1-w}\cos^2 Bt$  which appear in equations (10) and (11) as power series in  $w\cos^2 Bt$  by means of the binomial theorem. After these expansions are



performed, (10) becomes to terms of the 7th order in  $w$  :

$$\begin{aligned} & \frac{\ddot{\rho}}{B^2} [1 - 1.5w \cos^2 Bt + .375w^2 \cos^4 Bt + .0625w^3 \cos^6 Bt \\ & \quad + .02344w^4 \cos^8 Bt + .01172w^5 \cos^{10} Bt + .00682w^6 \cos^{12} Bt] \\ & + \rho [ .875 + 7.5w \cos^2 Bt - 4.125w^2 \cos^4 Bt + 1.9375w^3 \cos^6 Bt \\ & \quad + .96094w^4 \cos^8 Bt + .78516w^5 \cos^{10} Bt + .69830w^6 \cos^{12} Bt] \\ & + \rho [ -3w - 1.5w^2 \cos^2 Bt - 1.125w^3 \cos^4 Bt - .9375w^4 \cos^6 Bt \\ & \quad - .82031w^5 \cos^8 Bt - .73824w^6 \cos^{10} Bt] \\ & = [C - .875 + w - .0625w \cos^2 Bt - .015625w^2 \cos^4 Bt \\ & \quad - .007813w^3 \cos^6 Bt - .004882w^4 \cos^8 Bt \\ & \quad - .003417w^5 \cos^{10} Bt - .002563w^6 \cos^{12} Bt - .002016w^7 \cos^{14} Bt] \\ & \quad + sw^{\frac{1}{2}} \cos Bt [3 - 6w \cos^2 Bt + 3w^2 \cos^4 Bt] \\ & + \frac{\ddot{\rho}\rho}{B^2} [-3 + 3w \cos^2 Bt] + \rho^2 [-4.5w \cos^2 Bt \\ & \quad - 12w^2 \cos^4 Bt + 4.5w^3 \cos^6 Bt - 3w^4 \cos^8 Bt - 3w^5 \cos^{10} Bt] \\ & + \rho^2 [3w + 3w^2 \cos^2 Bt + 3w^3 \cos^4 Bt + 3w^4 \cos^6 Bt + 3w^5 \cos^8 Bt] \\ & \quad + s^2 [1.5 - 10.5w \cos^2 Bt + 16.5w^2 \cos^4 Bt - 7.5w^3 \cos^6 Bt] \\ & + \rho sw^{\frac{1}{2}} \cos Bt [-3 + 19.5w - 23.625w^2 \cos^4 Bt \\ & \quad + 5.4375w^3 \cos^6 Bt + .8672w^4 \cos^8 Bt]. \quad . \quad . \quad . \quad (12) \end{aligned}$$

Similarly, equation (11) becomes

$$\begin{aligned} & \frac{\ddot{s}}{B^2} + s = 3\rho w^{\frac{1}{2}} \cos Bt [1 - .5w \cos^2 Bt - .1250w^2 \cos^4 Bt \\ & \quad - .0625w^3 \cos^6 Bt - .03906w^4 \cos^8 Bt - .02734w^5 \cos^{10} Bt \\ & \quad - .02051w^6 \cos^{12} Bt] \\ & \quad + 3ws \cos^2 Bt + \rho^2 w^{\frac{1}{2}} \cos Bt [-6 + 7.5w \cos^2 Bt] \\ & \quad + s^2 [4.5w^{1/2} \cos Bt - 7.5w^{3/2} \cos^3 Bt] \\ & + \rho s [3 - 15w \cos^2 Bt] [1 - .5w \cos^2 Bt - .1250w^2 \cos^4 Bt \\ & \quad - .0625w^3 \cos^6 Bt - .0390w^4 \cos^8 Bt - .0273w^5 \cos^{10} Bt] \\ & \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13) \end{aligned}$$

Let us now assume that  $\rho$ ,  $s$ , and  $C$  can be expanded as  
*Phil. Mag.* S. 6. Vol. 44. No. 263. Nov. 1922. 3 K

power series in the constant of integration  $w$ , so that we may write \*

$$\begin{aligned}\rho &= \rho_1 w + \rho_2 w^2 + \rho_3 w^3 + \dots, \\ s &= w^{1/2} [s_1 w + s_2 w^2 + s_3 w^3 + \dots], \\ C &= C_0 + C_1 w + C_2 w^2 + C_3 w^3 + \dots,\end{aligned}$$

where the coefficients  $\rho_1, \rho_2, \rho_3, s_1, s_2, s_3$ , etc., are functions of the time not involving  $w$ , and  $C_0, C_1, C_2 \dots$  are purely numerical constants independent of  $w$ .

#### *Determination of Zero and First Order Terms in $w$ .*

Since the equations (12) and (13) hold for all values of  $w$ , the coefficients of the various powers of  $w$  in these equations must each vanish separately. There are no terms of order lower than  $w^{3/2}$  in equation (13), while if we equate to zero the terms in equation (12) which do not involve  $w$  i. e., coefficient of  $w^0$  we obtain  $C_0 = .875$ .

To determine the first-order term  $\rho_1$  we equate to zero the coefficient of the first-degree term in  $w$  in equation (12). We thus obtain

$$\frac{\ddot{\rho}_1}{B^2} + \frac{7}{8}\rho_1 = 1 - .03125[1 + \cos 2Bt] + C_1.$$

This gives on integration

$$\rho_1 = \rho_{01} + .010000 \cos 2Bt + D_1 \cos \left[ \sqrt{\frac{7}{8}}(Bt - \epsilon_1) \right],$$

where  $D_1$  and  $\epsilon_1$  are arbitrary constants and where

$$\frac{7}{8}\rho_{01} = .96875 + C_1.$$

It is necessary to set  $D_1 = 0$  in order to avoid introducing "Poisson terms" in the higher order coefficients  $\rho_2, s_2$ , etc. These terms are those of a type in which the time enters explicitly as well as through trigonometric functions (e. g.,  $t \cos \sqrt{\frac{7}{8}}Bt$ ), and would probably lead to very large perturbations, in which the distance of the electrons from the

\*  $C = \frac{p^2}{8me^2A}$  is a function of  $w$ , since the relation between the angular momentum  $p$  and the scale  $A$  of the model depends on the relative inclination of the two electron orbits. That the expansion of  $s$  involves fractional powers of the form indicated above follows from the fact that the expression for  $\ddot{s}B^{-2} + s$  in (13) contains terms of the form  $D\rho w^{n+\frac{1}{2}} \cos^{2n+1}Bt$  ( $D$  a purely numerical constant and  $n$  an integer). It is interesting to note that just such fractional power series in a parameter are frequently met with in lunar theory.

nucleus might tend asymptotically to the value infinity \*. Even if this difficulty were non-existent, the introduction of an extra frequency of vibration  $\sqrt{\frac{7}{8}} \frac{B}{2\pi}$  by setting  $D_1 \neq 0$  would lead to more complicated motions, an additional quantum number, and a negative energy content of smaller absolute value, none of which are characteristic of the normal state of the atom.

The values of  $\rho_1$  and  $C_1$  are determined by equating to zero the coefficient of  $w^{1/2}$  in equation (13). We thus obtain

$$\frac{\ddot{s}_1}{B^2} + s_1 = 3[\rho_{01} \cos Bt + \cdot 01 \cos 2Bt \cos Bt] = 3\rho_{01} \cos Bt + \cdot 015 [\cos Bt + \cos 3Bt],$$

whence for a periodic solution

$$\rho_{01} = -\cdot 005, \quad s_1 = E \cos (Bt - \epsilon_2) - \cdot 001875 \cos 3Bt.$$

The constant  $E$  may be set equal to zero, since we already have an arbitrary term in  $\cos Bt$  (viz., the term  $S = w^{1/2} \cos Bt$  corresponding to the unperturbed motion). The first terms in the expansion of  $\rho$ ,  $C$ , and  $s$  in terms of  $w$  are therefore

$$\begin{aligned} C &= \cdot 875000 - \cdot 973125w, \\ \rho &= [-\cdot 005000 + \cdot 010000 \cos 2Bt]w, \\ s &= (-\cdot 001875 \cos 3Bt)w^{3/2}. \quad \dots \quad (14) \end{aligned}$$

### *Determination of Higher Order Terms in $w$ .*

Making use of the relations given in (14) we can equate to zero the coefficients of  $w^2$  and  $w^{5/2}$  in equations (12) and (13) respectively, and so determine  $\rho_2$ ,  $C_2$ , and  $s_2$ . Knowing  $\rho_2$  and  $s_2$  we can determine third-order terms, and thus continue the process to any desired degree in  $w$ . The calculation of the first-order terms given above in detail is typical of the method used in computing the terms of higher order. With the aid of the trigonometric reduction formulas which express  $\cos^n Bt$  as a sum of linear trigonometric terms, the type forms obtained by equating to zero the

\* Cases, however, are sometimes found in dynamical theory where the Poisson and secular terms (in which the time appears explicitly) combine in such a way as to yield a conditionally periodic motion. Bohr has shown that when the perturbing potential has axial symmetry, the motion may be regarded as conditionally periodic if we consider only first-order terms in the perturbing field (Quantum Theory of Line Spectra, pp. 53-6), but this approximation is not sufficient in the present problem owing to the large amount of mutual action between electrons

coefficients of  $w^n$  and  $w^{n+1/2}$  in (12) and (13) respectively may be written:

$$B^{-2}\ddot{\rho}_n + \frac{7}{8}\rho_n - C_n = F_0 + F_1 \cos 2Bt + F_2 \cos 4Bt \dots \\ + F_n \cos 2nBt, \quad \dots \quad (15)$$

$$B^{-2}\ddot{s}_n + s_n - 3\rho_n \cos Bt = G_0 \cos Bt + G_1 \cos 3Bt \dots \\ + G_n \cos (2n+1)Bt, \quad \dots \quad (16)$$

where the F's and G's are purely numerical coefficients. The periodic solution of equations (15) and (16) is

$$\rho_n = \rho_{0n} + \rho_{1n} \cos 2Bt + \rho_{2n} \cos 4Bt \dots + \rho_{nn} \cos 2nBt,$$

$$s_n = s_{1n} \cos 3Bt + s_{2n} \cos 5Bt \dots + s_{nn} \cos (2n+1)Bt,$$

$$C_n = \frac{7}{8}\rho_{0n} - F_0,$$

where

$$-\rho_{0n} = \frac{1}{2}\rho_{1n} + \frac{1}{3}G_0, \quad \rho_{jn} = \frac{F_j}{(\frac{7}{8} - 4j^2)}, \quad (j \neq 0),$$

$$s_{jn} = \frac{G_j + \frac{3}{2}(\rho_{jn} + \rho_{(j+1)n})}{1 - (2j+1)^2}.$$

$\rho_{1n}, \rho_{2n}, \dots, \rho_{nn}$  are thus determined by equating to zero the coefficients of  $\cos 2Bt, \cos 4Bt, \dots, \cos 2nBt$  respectively in equation (15), while  $s_{1n}, s_{2n}, \dots, s_{nn}$  are found by equating to zero the coefficients of  $\cos 3Bt, \cos 5Bt, \dots, \cos (2n+1)Bt$  respectively in (16).  $\rho_{0n}$  is determined by equating to zero the coefficient of  $\cos Bt$  in (16), thus avoiding the necessity for introducing in the expression for  $s_n$  the Poisson term  $Gt \cos Bt$  ( $G$  some constant), in which the time enters explicitly.

### Final Determination of Orbits.

Following this method of attack, we obtain for the final result:—

$$\rho = [ -\cdot 005000w - \cdot 003643w^2 - \cdot 002386w^3 - \cdot 001504w^4 \\ - \cdot 000887w^5 - \cdot 000386w^6 - \cdot 000024w^7 + \dots ] \\ + [ \cdot 010000w + \cdot 009592w^2 + \cdot 008435w^3 + \cdot 007450w^4 \\ + \cdot 006632w^5 + \cdot 005799w^6 + \cdot 005038w^7 ] \cos 2Bt \\ + [ \cdot 002507w^2 + \cdot 003175w^3 + \cdot 003300w^4 + \cdot 003177w^5 \\ + \cdot 002988w^6 ] \cos 4Bt \\ + [ \cdot 0004134w^3 + \cdot 0007303w^4 + \cdot 0009320w^5 \\ + \cdot 0010386w^6 ] \cos 6Bt \\ + [ \cdot 0000811w^4 + \cdot 0001825w^5 + \cdot 0002760w^6 ] \cos 8Bt \\ + [ \cdot 0000169w^5 + \cdot 0000465w^6 ] \cos 10Bt + \cdot 0000036w^6 \cos 12Bt,$$





the power series development in the parameter  $w$ . For  $w=0$ , the perturbations  $\rho$  and  $s$  vanish, and  $C=.875$ ; this is an exact solution, which is nothing else than the Bohr helium atom, in which the two electrons move in the same plane. As the constant of integration  $w$  is given increasing values, the orbits intersect each other at greater angles, and the perturbations become larger.

### *Evaluation of Energy.*

After the orbits have been determined, the next step is to compute the energy, so that the ionization potential may be calculated. If we eliminate  $\dot{\phi}$  by means of the relation (3) and use the reduced units of (7), the expressions for the kinetic and potential energies given in equations (1) and (2) become

$$T = \frac{2e^2}{A} \left[ \frac{(\dot{r}^2 + \dot{\zeta}^2)}{B^2} + \frac{C}{r^2} \right],$$

$$V = \frac{e^2}{A} \left[ \frac{1}{2r} - \frac{4}{\sqrt{r^2 + \zeta^2}} \right].$$

Next, making use of the relations  $r = \eta + \rho$ ,  $\zeta = S + s$ , expand the various powers of  $r$  and  $\zeta$  as power series in the perturbations  $\rho$  and  $s$ , neglecting terms of third and higher orders. This gives

$$\begin{aligned} T = \frac{2e^2}{A} \left[ 1 + \frac{C-1+w}{\eta^2} + \frac{1}{B^2} (2\eta\dot{\rho} + 2S\dot{s} + \dot{s}^2 + \dot{\rho}^2) \right. \\ \left. + \frac{C}{\eta^2} \left( -\frac{2\rho}{\eta} + \frac{3\rho^2}{\eta^2} \right) \right], \\ V = \frac{2e^2}{A} \left[ -2 + \frac{1}{4\eta} - \frac{\rho}{4\eta^2} + \frac{\rho^2}{4\eta^3} + (2Ss + 2\eta\rho + \rho^2 + s^2) \right. \\ \left. - 3(\rho^2\eta^2 + 2\eta S\rho s + S^2s^2) \right]. \end{aligned}$$

If  $w=0$ , so that the two electrons move in the same plane,  $\rho=s=0$  and  $C=.875$ ; the above expressions then reduce to

$$T = \frac{7e^2}{4a}, \quad V = -\frac{7e^2}{2a},$$

so that we have the familiar expressions for the energy of the Bohr helium atom. We thus see that practically all the terms in the above expressions for the energy are perturbative terms of small magnitude.

The next step is to write  $\rho$  and  $s$  in the form

$$\begin{aligned}\rho = & a_0 + a_1 \cos 2Bt + a_2 \cos 4Bt + a_3 \cos 6Bt + a_4 \cos 8Bt \\ & + a_5 \cos 10Bt + a_6 \cos 12Bt, \\ s = & b_3 \cos 3Bt + b_5 \cos 5Bt + b_7 \cos 7Bt,\end{aligned}$$

where the coefficients  $a_0, a_1, \dots, a_6, b_3, b_5, b_7$ , are power series in  $w$  given in equation (17). Also using the binomial theorem we may expand the various powers of  $\eta = \sqrt{1-w} \cos^2 Bt$  as power series in  $w \cos^2 Bt$ . If the series occurring in products be multiplied together,  $T$  and  $V$  will consist of terms which are products of powers of sines and cosines of integral multiples of  $Bt$ . By means of the addition formulas the products of powers of sines and cosines may be reduced to sums of linear trigonometric terms, thus giving  $T$  and  $V$  as Fourier series in the time, so that

$$\begin{aligned}T &= T_0(w) + T_1(w) \cos 2Bt + T_2(w) \cos 4Bt + \dots \\ V &= V_0(w) + V_1(w) \cos 2Bt + V_2(w) \cos 4Bt + \dots\end{aligned}$$

It is only necessary to actually evaluate the constant term in this final Fourier expansion, as the periodic terms will cancel out when  $T$  and  $V$  are added together to obtain the total energy, which is constant. After reduction to power series form in  $w$ , the constant parts  $T_0$  and  $V_0$  of the kinetic and potential energies prove to be

$$T_0 = \frac{e^2}{A} [1.750 - .053750w - .028650w^2 - .019062w^3 - .013920w^4 - .010658w^5 - .008473w^6 - .006938w^7], \quad (19)$$

$$V_0 = -\frac{2e^2}{A} [1.750 - .053750w - .028650w^2 - .019046w^3 - .013884w^4 - .010613w^5 - .008439w^6 - .006839w^7], \quad (20)$$

while the total energy  $W$  is  $T_0 + V_0$ .

### Check on Accuracy of Solution.

One of the standard methods of checking the accuracy of computations in Astronomy is to compute the energy and see if it remains constant. This method could be used in our problem, but would involve the calculation of the coefficients of the various periodic terms in the Fourier expansions of  $T$  and  $V$ , which would be extremely laborious, as over twenty pages of computations are required to determine the constant term alone. A much easier method of checking is furnished by the fact that in motion under the

inverse square law the average absolute value of the potential energy is twice the average kinetic energy \*. Since the average value is simply the constant part of the Fourier expansion, and since a power series development is unique, the coefficients of like powers of  $w$  in the bracketed power series in equations (19) and (20) must, therefore, be identical if the computations are correct. There is absolute agreement in the first three terms, while the small errors in the fifth decimal place in subsequent terms are insignificant, and due mostly to neglect of third and higher powers of the perturbations.

### PART III.—APPLICATION OF QUANTUM CONDITIONS TO MODEL WITH AXIAL SYMMETRY.

The same value for the energy is given consistently by several different types of quantum conditions, viz., the value obtained by choosing the constants of integration ( $p$  and  $w$ ) so as to satisfy the relations

$$p = \frac{n_2 h}{2\pi}, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$\bar{T} = \frac{h}{2} (n_1 \nu_1 + n_2 \nu_2), \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where  $n_1$  and  $n_2$  are integers,  $\bar{T}$  is the average value of the kinetic energy (equal to the negative of the total energy), and  $\nu_1$ ,  $\nu_2$  are the two intrinsic frequencies of vibration, given by †

$$\begin{aligned} \nu_1 &= \frac{B}{2\pi}, \text{ the frequency of vibration of the coordinates } r \text{ and } z, \\ \nu_2 &= \frac{\dot{\phi}}{2\pi}, \text{ the frequency of rotation of the cyclic coordinate } \phi \\ &(\text{i. e., } \frac{1}{2\pi} \text{ times the mean angular velocity of the electrons} \\ &\text{about the axis of symmetry}). \quad . \quad . \quad . \quad . \quad . \quad (23) \end{aligned}$$

Equation (21) states that the resultant angular momentum

\* For proof of this relation, see Sommerfeld, 'Atombau und Spektrallinien,' 2nd ed., p. 472.

† For proof that the  $\nu_1$  and  $\nu_2$  defined in (23) are the intrinsic frequencies in the Fourier expansion of the Cartesian coordinates  $x$ ,  $y$ ,  $z$ , see Bohr, 'The Quantum Theory of Line Spectra,' p. 33.



$p$  must be an integral multiple of  $\frac{h}{2\pi}$ . In the actual numerical determination of the orbits so as to satisfy (21) and (22),  $T$  and  $v_2$  were evaluated as the constant terms in Fourier expansions. The quantum numbers  $n_1$  and  $n_2$  were each taken equal to unity to give the normal orbits, those of lowest energy. The value of  $w$  was found by trial and error to be .7216, giving an energy of 74.9 volts, already discussed. The remaining pages will be concerned with showing that various theories devised for quantizing the stationary states demand that equations (21) and (22) be satisfied.

### Sommerfeld Quantum Conditions.

From the standpoint of the Sommerfeld conditions (viz., that  $\int p_i dq_i = n_i h$ ) the result (21) is obtained by assuming that the cyclic coordinate  $\phi$  together with its conjugate momentum  $p$  satisfy a quantum integral, so that

$$\int_0^{2\pi} p d\phi = n_2 h.$$

This is in agreement with Epstein's theory that when partial separation of variables can be effected in the Hamilton-Jacobi equation, the Sommerfeld conditions should be satisfied by the phase integrals associated with the coordinates which can be separated\* (i. e.,  $\int p_i dq_i = n_i h$  for the particular values of  $i$  for which  $p_i$  may be regarded as a function of  $q_i$  only)†.

Also, as mentioned by Bohr ‡, the value  $\frac{n_2 h}{2\pi}$  for the resultant angular momentum appears to be demanded by the conservation of angular momentum, independently of quantum theory considerations.

For a conditionally periodic system with any number of

\* *Verh. d. D. Phys. Ges.* vol. xix. p. 127.

† It is interesting to note that Epstein's conditions demand that the resultant angular momentum of any three body system, and hence of any model of helium (not necessarily in the normal state) be equal to an

integral multiple of  $\frac{h}{2\pi}$ , for in this much more general case the resultant angular momentum can be proved conjugate to a cyclic coordinate of period  $2\pi$ . (For proof, see Whittaker, 'Analytical Dynamics,' p. 345.)

‡ 'The Quantum Theory of Line Spectra,' p. 35 (*Mémoires Dan. Acad.* 1918).

degrees of freedom \*, which has two intrinsic frequencies of vibration  $\nu_1$  and  $\nu_2$ , and in which separation of variables can be effected, the Sommerfeld quantum conditions demand that the average value of the kinetic energy be that given in equation (22) †. The general type of motion in the particular dynamical system we are considering is presumably not conditionally periodic, but, instead, the great majority of orbits seem to be characterized by large perturbations, in which the radius may tend steadily, though very slowly, to the value zero or infinity. For this type of motion the Sommerfeld quantum integrals have no meaning (except in case of the cyclic coordinate  $\phi$ ) and no technique appears to have been devised for quantizing the general orbits in dynamical systems of this character. However, the simple relation given in (22), though not often mentioned in the literature, is one which is satisfied in practically all cases in which quantum theory dynamics have been applied successfully, and consequently may itself be regarded as a quantum condition of considerable generality. Therefore, when particular classes of orbits can be found which are conditionally periodic and characterized by two intrinsic frequencies of vibration, one would expect this relation to be satisfied. This amounts to saying that, since orbits characterized by constantly increasing perturbations cannot occur in the normal state, we need quantize only the families of orbits which are conditionally periodic, which contain two intrinsic frequencies and four arbitrary constants (two of which are epoch angles), and which therefore resemble the general motion in a conditionally periodic system with two degrees of freedom ‡.

\* If the number of degrees of freedom exceeds two, the motion is partially "degenerate."

† To prove this the case we observe that by Euler's theorem on homogeneous quadratic functions

$$T = \frac{1}{2} \sum_i \frac{\partial T}{\partial q_i} \dot{q}_i = \frac{1}{2} \sum_i p_i \dot{q}_i, \text{ since } p_i = \frac{\partial T}{\partial \dot{q}_i}.$$

The relation  $\bar{T} = \frac{h}{2} (n_1 \nu_1 + n_2 \nu_2)$  is obtained immediately by taking time average and using the facts that  $\int p_i dq_i = n_i h$  and that the frequency of  $q_i$  is either  $\nu_1$  or  $\nu_2$ .

‡ If the Poisson and secular terms in which the time appears explicitly should prove to combine in such a way as to make the general motion conditionally periodic, then, if separation of variables could be effected, the Sommerfeld quantum conditions could be applied directly and the general motion could be specified with the aid of three angle variables. The relation (22) would then be obtained by equating to zero the quantum number  $n_3$  associated with the third intrinsic frequency  $\nu_3$  not appearing in the particular family of orbits studied in solving the dynamical problem.

*Schwarzschild Angle Variables.*

The "angle variables" (Winkelkoordinaten) are intrinsic coordinates which are  $2\pi t$  times the frequencies of vibration of the system, and thus possess the characteristic properties of being linear functions of the time such that alteration of any one of them by an amount  $2\pi$  leaves the configuration of the dynamical system unaltered. The two angle variables for the family of orbits given in equations (17) and (18) are therefore  $2\pi\nu_1 t$  and  $2\pi\nu_2 t$ , where  $\nu_1$  and  $\nu_2$  have the values given in (23). The intrinsic momenta  $P_1$  and  $P_2$  conjugate to the angle variables  $Q_1$  and  $Q_2$  are constants defined by the canonical equations

$$\frac{dQ_1}{dt} = \frac{\partial H}{\partial P_1}, \quad \frac{dQ_2}{dt} = \frac{\partial H}{\partial P_2},$$

where  $H$  is the Hamiltonian function (*i. e.*, the energy regarded as a function of  $P_1$  and  $P_2$ ). The general solution of the above equations can be shown to be \*

$$P_1 = \frac{1}{2\pi} \int_0^{2\pi} 2m[\dot{R}^2 + \dot{Z}^2] dt,$$

$$P_2 = \frac{1}{2\pi} \int_0^{2\pi} p d\phi = p.$$

Equations (21) and (22) follow immediately on setting  $P_1$  and  $P_2$  equal to integral multiples of  $\frac{h}{2\pi}$  in accordance with Schwarzschild's quantum conditions, which demand that

$$\int_0^{2\pi} P_i dQ_i = n_i h.$$

*Ehrenfest's Adiabatic Hypothesis.*

Ehrenfest's adiabatic hypothesis states that motions "allowed" by the quantum theory are transformed into new "allowed" motions as the character of the dynamical system is altered by changing very slowly some parameter appearing in the energy. We shall take this parameter  $a$  proportional to the perturbative force of repulsion between

\* For proof, use methods of Epstein (*Ann. d. Phys.* vol. li. p. 168).

the two negative electrons, so that the total potential energy  $V$  of the system is

$$V = -\frac{4e^2}{\sqrt{R^2 + Z^2}} + \frac{ae^2}{2R} \quad (\text{cf. equation (2)}).$$

For  $a=0$  there is no mutual action between negative electrons, and then each electron describes a circle or ellipse characteristic of a central force obeying the inverse square law. Since the motion in this undisturbed system is periodic, the action integral must be an integral multiple of  $h$ , so that we have

$$2 \int_0^\tau T dt = (n_1 + n_2)h, \quad . \quad . \quad . \quad . \quad (24)$$

where  $\tau$  is the period. Also we shall assume that the resultant angular momentum about the axis of symmetry is

an integral multiple of  $\frac{h}{2\pi}$ , which apparently is demanded by

the conservation of angular momentum, and which is required if Sommerfeld's quantizing of space in polar coordinates is accepted. Now let the parameter  $a$  be increased from the fictitious value zero to the actual value unity. Since there are no forces operative which have a moment about the axis of symmetry, the resultant angular momentum retains its original value  $\frac{n_2 h}{2\pi}$ , and the axial symmetry is preserved.

Also if we assume that the motion always remains conditionally periodic as the perturbing field is thus gradually increased, then, using an equation given by Ehrenfest\*, it is readily shown that the average kinetic energy has the value demanded by (22).

### *Bohr's Quantum Conditions.*

By quantizing the perturbations in a manner analogous to that of the Sommerfeld conditions for conditionally periodic motions, Bohr has devised a general method for determining the "allowed" motions whenever the perturbing potential has axial symmetry†, although his treatment is intended primarily for cases where the departures from the undisturbed orbits are so small that only first powers in the perturbations need be considered. These quantum conditions demand that

\* *Ann. d. Phys.* vol. li. p. 348, equation (m).

† 'The Quantum Theory of Line Spectra,' pp. 53-6.



the angular momentum about the axis of symmetry be an integral multiple of  $\frac{h}{2\pi}$ \*, and that the motion be adiabatically derivable from an unperturbed orbit for which the action integral has the value given in (24). Bohr's conditions are therefore in agreement with the application of the Ehrenfest adiabatic hypothesis given above.

Jefferson Physical Laboratory,  
Harvard University.  
March 13, 1922.

*Note.*—Since this paper was written, an article by Bohr has appeared in the *Zeitschrift für Physik*, vol. ix. (1922), p. 1, in which he conjectures that the Kemble model with axial symmetry and with crossed orbits (studied in the present paper) may be the correct solution of the normal helium atom. It is therefore to be regretted that calculation has given an ionization potential of 20.7 volts instead of 25.4 demanded by experiment.

According to Bohr the normal helium atom is capable of formation from a free electron and ionized helium atom by continuous transition through a series of intermediate orbits. The family of orbits in the present by varying the constants of integration  $p$  and  $w$  furnish a means of transition from the Kemble model to a stationary state of lower energy given by

$w=0$  and  $p=\frac{h}{\pi}$ , which gives the coplanar circular orbits of the original Bohr helium model. According to Bohr (p. 32) this model cannot be formed by a continuous transition from the stationary states found in the orthohelium model (coplanar orbits of unequal size), but the statement which I have just made makes it appear capable of formation by continuous transition from the stationary states of the parhelium series. The instability which may result from the possibility of degeneration into coplanar orbits of lower energy makes it plausible that the normal state of the helium atom may not be characterized by crossed orbits with axial symmetry.

\* Bohr's conditions demand that the resultant angular momentum of a single electron about the axis of symmetry be  $\frac{n_2 h}{2\pi}$ , while in our conditions this value was taken for the resultant angular momentum of both electrons, a quantity twice as great. This, however, is probably not a contradiction, as Bohr's method was derived for systems with only one electron.

LXXIII. *The Use of a Triode Valve in registering Electrical Contacts.* By G. A. TOMLINSON, B.Sc.\*

A THREE electrode valve can be applied with advantage to certain forms of apparatus in which use is made of electrical contacts. A common case is that of a relay in which it is usual to cause a feeble movement of one instrument to make a contact and close the circuit of a second comparatively powerful instrument supplied from an independent source. An improvement in several respects can be made if the first contact is placed in the grid circuit of a valve, and the second instrument is connected in the anode circuit and is operated by the anode current.

An arrangement used by the writer is shown in fig. 1.

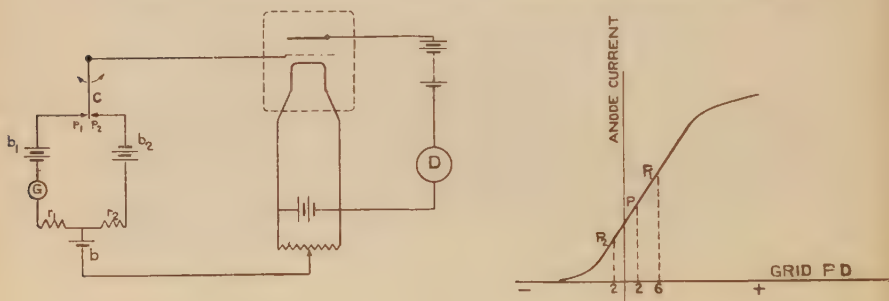


FIG 1

A small tongue of platinum C is moved by the first instrument between two platinum points  $p_1$  and  $p_2$ , and on making contact either raises or lowers the potential of the grid by about 4 volts by introducing the batteries  $b_1$  or  $b_2$ .

The reaction on the anode current, which is illustrated by the diagram of the valve characteristic, operates the instrument D. Thus the points  $P_1$  and  $P_2$  show the anode current when the tongue is in contact at  $p_1$  and  $p_2$ , the difference being the range of current available, which is about 3 milliamperes. The actual values of the grid potential are adjusted by the battery  $b$  to vary between  $-2$  and  $+6$  volts, to obtain the best range of anode current.

In this particular case the relay is required only to detect small angular movements of an instrument in either direction from the zero position, and the instrument used in the anode circuit is a pivoted moving-coil galvanometer.

\* Communicated by the Director of the National Physical Laboratory.

The resistances  $r_1$  and  $r_2$  in the circuit enable a fine adjustment of the points  $p_1$  and  $p_2$  to be made. These points can be advanced by micrometer screws until both just touch the platinum tongue. This contact can be observed by temporarily inserting the galvanometer  $G$  in the circuit. The E.M.F.'s of the batteries  $b_1$  and  $b_2$  act in the same direction in this local circuit, and with suitable resistances  $r_1$  and  $r_2$  a small local current flows when  $p_1$  and  $p_2$  are both in contact. The points can then be separated by any desired amount. The resistances  $r_1$  and  $r_2$  also prevent a short circuit if an accidental contact is made from  $p_1$  to  $p_2$ .

A relay of this type has several advantages. The current to be transmitted through the contacts is very small, being only the grid current of the valve. Variation in the resistance of the contact within wide limits has no effect on the action, owing to the great resistance already in the circuit between the grid and the filament. The amplification of mechanical power, which is the function of a relay, is provided for by the electrical amplifying properties of the valve. A further advantage, that may be important in some cases, is that this relay may be operated by much weaker forces than could be used with an ordinary relay. In the latter type the contact is placed directly in the circuit of the second instrument, and a certain contact pressure is necessary to ensure the passage of sufficient operating current. With the valve relay an extremely light contact between clean platinum surfaces is sufficient to charge the grid of the valve, and very weak forces will therefore work the relay in a satisfactory way. Thus it has been found that a contact force of 0.000001 grm. is quite sufficient to charge the grid and produce the required change in the anode current. Since there is practically no current transmitted by the contacts, there is no objectionable coherence of the surfaces, and the movement of the contact tongue can be reduced to a very small amount if desired. For example, the relay has been operated with the travel of the tongue only about 1/1000 mm.

Certain modifications to meet different requirements may be suggested. If the contact is for any reason intermittent, a comparatively steady current may be obtained in the anode circuit by connecting a suitable condenser across the grid and filament. A high-resistance grid-leak may be used if it is desirable for the anode current to assume its normal value immediately the contact in the grid circuit is broken.

The writer has also made some experiments, using an electrical contact in the way described for quite a different

purpose, namely as an indicator for precise measurement. A compound lever with a magnification of about 600 was arranged to be moved by a micrometer at the one end, and carried the contact at the other end. Using this to measure the thickness of a parallel slip-gauge with the lower face resting on three steel balls and the contact on the upper face, it was found that repetition of observations could easily be obtained with variations not exceeding  $0.5 \times 10^{-6}$  inch. These experiments indicate that the advantages obtained by making contact in the grid circuit of a valve may eliminate some of the difficulties hitherto experienced in this method of measurement.

This method appears to have advantages in connexion with the reception of feeble wireless signals with the aid of a relay; and it is also proposed to try it, on account of its freedom from sparking at the grid-circuit contact, in connexion with the location of the height of the mercury surface in the vacuum space of a standard barometer.

July 1922.

LXXIV. *Radiative Equilibrium: the Insolation of an Atmosphere.* By E. A. MILNE, M.A., Fellow of Trinity College, Cambridge\*.

§ 1. *INTRODUCTION.*—The generally accepted theory of the existence of the earth's stratosphere was put forward in 1908 by Gold†. Gold showed that when radiation processes were taken into account the continued existence of an adiabatic gradient to indefinitely great heights was impossible; for the upper portions of such an atmosphere, being very cold, would radiate very little, but on the other hand, being backed by an extensive cushion of warmer air besides the warm surface of the earth, would be subjected to low-temperature radiation of considerable intensity, and the consequent excess of absorption over emission would raise their temperature and so disturb the adiabatic gradient. Such upper portions, however, could not exchange heat with the rest of the atmosphere by convection, for they would tend to rise, not fall. Consequently

\* Communicated by the Author.

† "The Isothermal Layer of the Atmosphere and Atmospheric Radiation," *Proc. Roy. Soc.* 82 A. p. 43 (1909). A preliminary announcement was made at the British Association meeting in 1908; see 'Nature,' vol. lxxviii. p. 551 (1908). See also *Geophysical Memoirs*, No. 5 (Met. Office), vol. i. p. 65 (1913).



their temperature would continue to increase until the extra emission due to increased temperature balanced the absorption and a new steady state set in—a state of radiative equilibrium. The direct absorption of solar radiation is small and, though important, does not affect the argument. (It is of interest to mention that exactly the same course of argument shows that even in the absence of convection a strictly isothermal atmosphere is impossible; for the outer portions would not be able to absorb as much as they emitted, and so would cool, causing convection.)

Gold embodied these ideas in analysis, in order to determine the temperature and the height of the tropopause, and he showed that the theory generally was adequate to account for the observed values. His procedure, however, was in part empirical. In the light of Schwarzschild's\* theory of radiative equilibrium in a stellar atmosphere, an immediate rough evaluation of the boundary temperature is possible; if  $T_0$  is this temperature, then  $T_0^4 = \frac{1}{2}T_1^4$ , where  $T_1$  is the effective temperature of the system (earth plus atmosphere) as determined by the amount of energy radiated away into space. This energy is equal to the mean value of the absorption of solar radiation, assuming that the earth is on the average neither losing nor accumulating energy. The value of  $T_1$ , deduced by Abbot† from the solar constant and the earth's albedo, is about  $254^\circ$ , giving  $T_0 = 214^\circ$ . The observed mean value of the temperature of the stratosphere over the British Isles is about  $219^\circ$ . Schwarzschild's formula,  $T_0^4 = \frac{1}{2}T_1^4$ , was indeed obtained independently by Humphreys‡ in this connexion, and applied to the stratosphere. Gold, however, did not proceed in this way. Accepting the observed division of the atmosphere into two shells—an inner one in convective equilibrium with a known temperature gradient, and an outer one at a uniform temperature,—he determined the height at which the convective gradient should terminate, in order that the atmosphere above this height should, as a whole, gain as much heat by absorption as it lost by radiation; the temperature of the convective region at this height then gave the temperature of the isothermal region. It appeared that a satisfactory balance was obtained if the point of division was taken at a height given by  $p = \frac{1}{4}p_1$ , where  $p$  is the pressure at any height,  $p_1$  the ground-pressure. It appeared further that there was very nearly a balance of radiation in the upper

\* *Gött. Nach.* 1906, p. 41.

† *Annals Astrophys. Obs. Smithsonian. Inst.* ii. p. 174 (1908). 'The Sun' (Appleton, New York, 1912), p. 323.

‡ *Astrophys. Journ.* vol. xxix. p. 26 (1909).

layer of the convective region extending from  $p = \frac{1}{2}p_1$  to  $p = \frac{1}{4}p_1$ , from which Gold deduced that in this layer the convection would be small.

It is the object of this paper to point out a certain difficulty in Gold's work, and to consider an idealized problem which is suggested by it in the absorption of radiation by an atmosphere subject to insolation.

Since the paper was first written, the author has become aware of a paper by Emden\* which anticipates portions of it. Emden criticized Gold's theory on certain points, and investigated the general theory of the radiative equilibrium of an atmosphere by a method similar to that of the present paper. Where necessary, the paper has been recast to take account of Emden's work.

§ 2. *Criticism of Gold's solution.*—One of the most interesting points in Gold's discussion is his isolation and explicit formulation of the condition for a convective atmosphere. In such an atmosphere, transfers of energy are being effected both by radiation and by convection, and across any plane there will be a net radiative flux and a convective flux. Now convection can only transfer heat upwards, not downwards. But assuming a steady state, the upward convective flux plus the net radiative flux must be equal to the downward solar flux. Hence *the net radiative flux (as due to the earth and atmosphere together) must be less than the downward solar flux.* But the downward solar flux at any point cannot exceed its value at the boundary: and at the boundary the downward solar flux must be equal to the outward flux due to the earth and atmosphere. Hence another form of the condition is: *the net outward flux across any plane must be less than its value at the boundary.* Again, the upper layers must be gaining more heat by convection from below than they are losing to layers above. Hence, for a steady state, *emission of radiation must exceed absorption in the upper layers* (for emission must equal absorption plus net gain by convection). Whenever these inequalities become equalities, radiative equilibrium holds; if they become reversed the state cannot be a steady one, for it would involve convection downwards†.

\* "Über Strahlungsgleichgewicht und atmosphärische Strahlung: ein Beitrag zur Theorie der oberen Inversion," *Sitz. d. K. Akad. Wiss. zu München*, 1913, pp. 55–142.

† Gold's conditions have been applied by the writer to stellar atmospheres in a paper recently communicated to the Royal Society.

Now Gold applied these conditions in various ways to show under what circumstances a convective atmosphere can or cannot exist: *e. g.*, he showed that a convective atmosphere cannot extend indefinitely, yet must extend above  $p = \frac{1}{2} p_1$ . But he did not point out that his final solution was inconsistent with these conditions. We shall show that although on the assumptions made the layer  $(\frac{1}{4} p_1, 0)$  is neither gaining nor losing heat as a whole, yet its upper portions are emitting more than they are absorbing, and its lower portions absorbing more than they are emitting; consequently the upper layers must cool and sink, the lower ones warm and rise, convection will occur, and the state of isothermal equilibrium must be destroyed. Further, although the layer  $(\frac{1}{2} p_1, \frac{1}{4} p_1)$  satisfies the conditions for convective equilibrium as a whole, emission exceeding absorption, in the upper portions absorption exceeds emission, so that a steady convective state in this region is not possible: the smallness of the excess of emission over absorption for the whole layer, attributed by Gold to the slightness of convection required, is merely the result of the excess in the lower portions being balanced by the deficiency in the upper ones.

Actually we can prove a more precise result than this, under very general conditions. We shall show that the excess of absorption over emission at the base of Gold's isothermal layer, per unit optical mass, is numerically equal to the excess of emission over absorption at the top, whatever the temperature distribution in the convective layer and whatever the law connecting the coefficient of absorption with height. To do this we shall employ the approximate form of the equations of transfer of radiant energy. It may be mentioned here that though Gold uses the exact formulæ (involving  $Ei$  functions) which take full account of the spherical divergence of the radiation, his results can be obtained more simply to the same degree of precision by using the approximate formulæ and by making free use of the optical thickness and the net flux of radiation. The quite small errors of the approximate formulæ are swallowed up in the uncertainty of the numerical data that have finally to be employed. The uncertainty arises in the final translation of the optical thicknesses into actual thicknesses; but, as in other cases of radiative equilibrium, many of the results hold in a form independent of the numerical values of the absorption coefficients.

Let  $\tau$  be the optical thickness measured *inwards* from the

outer limit of the atmosphere ; if  $\rho$  is the density at height  $h$ ,  $k(h)$  the mass-absorption coefficient, then

$$\tau(h) = \int_h^\infty k(h) \rho dh.$$

Let  $I(\tau)$  be the intensity of radiation at  $\tau$  in a direction  $\theta$  with the outward vertical, where  $0 < \theta \leq \frac{1}{2}\pi$ ; and let  $I'(\tau)$  be the intensity at  $\psi$  with the inward vertical, where  $0 \leq \psi \leq \frac{1}{2}\pi$ . Assume the material is *grey* (i.e. has an absorption coefficient the same for all the wave-lengths that are important—in this case the wave-lengths that are predominant in the low-temperature radiation considered). Let  $B(\tau)$  be the intensity of black body radiation for the temperature ruling at the point  $\tau$ ; and let  $\pi F(\tau)$  be the net upward flux of energy per unit area across a horizontal plane at  $\tau$ . Then

$$\cos \theta \frac{dI}{d\tau} = I - B, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\cos \psi \frac{dI'}{d\tau} = B - I', \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{1}{2}F(\tau) = \int_0^{\frac{1}{2}\pi} I(\tau) \sin \theta \cos \theta d\theta - \int_0^{\frac{1}{2}\pi} I'(\tau) \sin \psi \cos \psi d\psi. \quad . \quad . \quad . \quad (3)$$

Consider the expression

$$\pi F(\tau') - \pi F(\tau''), \quad (\tau' > \tau'').$$

Here  $\pi F(\tau')$  is the net amount of radiant energy entering the lower boundary of the layer  $(\tau', \tau'')$ ,  $\pi F(\tau'')$  the net amount leaving the upper boundary. Hence *the difference is the excess of absorption over emission for the whole layer*  $(\tau', \tau'')$ . Thus  $F(\tau)$  behaves as an integral, whether or no radiative equilibrium holds; this is interesting, for in certain forms of radiative equilibrium it appears naturally as an integral\* of (1) and (2) in the form  $F = \text{const.}$

Let  $\tau_1$  be the value of  $\tau$  at the earth's surface. Now suppose with Gold that the complete atmosphere  $\tau = 0$  to  $\tau = \tau_1$  consists of two shells—an outer one at a uniform temperature from  $\tau = 0$  to  $\tau = \tau_2$  (say), and an inner one in convective equilibrium from  $\tau = \tau_2$  to  $\tau = \tau_1$ . Then the outer one will be in radiative equilibrium as a whole, provided

$$F(\tau_2) - F(0) = 0, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and this is the equation which determines  $\tau_2$ .

\* Monthly Notices, lxxxi. p. 362 (1921).

We now approximate. Setting  $t = 2\tau$ ,  $t_1 = 2\tau_1$ , etc., and using  $t$  as the variable specifying position, equations (1), (2), (3) can be written approximately \*

$$\frac{dI}{dt} = I - B, \quad \frac{dI'}{dt} = B - I', \quad . . . (5), (6)$$

$$F(t) = I(t) - I'(t), \quad . . . . . (7)$$

and the equation for  $t_2$  is

$$I(t_2) - I'(t_2) - I(0) = 0, \quad . . . . . (8)$$

since the incident radiation  $I'(0)$  is zero †. Solving (5) and (6) with the assumption that the air near the ground has the same temperature as the ground and that the earth radiates like a black body, we find

$$I(t) = e^t \int_t^{t_1} B(t) e^{-t} dt + B(t_1) e^{-(t_1-t)}, \quad . . . (9)$$

$$I'(t) = e^{-t} \int_0^t B(t) e^t dt. \quad . . . . . (10)$$

These can be inserted in (8), and  $t_2$  determined as soon as  $B(t)$  is known as a function of  $t$  in the convective region.

Now the excess of absorption over emission in a small element of volume  $dv$  is

$$\begin{aligned} k\rho dv \left[ \int I d\omega + \int I' d\omega' - 4\pi B \right] \\ = 2\pi k\rho dv \left[ \int_0^{\frac{1}{2}\pi} I \sin \theta d\theta + \int_0^{\frac{1}{2}\pi} I' \sin \psi d\psi - 2B \right] \\ = 2\pi k\rho dv [I(t) + I'(t) - 2B(t)] \end{aligned}$$

approximately. Denote the expression in square brackets by  $E(t)$ . Then for the values of the excess of absorption over emission at the top and bottom of the isothermal region we have respectively

$$E(0) = I(0) - 2B(0),$$

$$E(t_2) = I(t_2) + I'(t_2) - 2B(t_2), \quad . . . (11)$$

or, using (8),

$$E(0) = I(t_2) - I'(t_2) - 2B(0). \quad . . . (12)$$

\* For details, see *e. g.* Monthly Notices, lxxxi. p. 363 (1921).

† Ignoring solar radiation. See below.



We shall now prove that  $I(t_2) = 2B(t_2)$ . From (9), remembering that  $B$  is constant in  $(t_2, 0)$ , we have

$$I(t_2) = e^{t_2} \int_{t_2}^{t_1} B(t) e^{-t} dt + B(t_1) e^{-(t_1-t_2)},$$

$$I(0) = \int_{t_2}^{t_1} B(t) e^{-t} dt + B(t_2)(1 - e^{-t_2}) + B(t_1) e^{-t_1},$$

whence

$$I(0) - e^{-t_2} I(t_2) = B(t_2)(1 - e^{-t_2}).$$

Further, from (10),

$$I'(t_2) = B(t_2)(1 - e^{-t_2}). \quad . \quad . \quad . \quad (13)$$

Inserting in the equation for  $t_2$ , namely (8), we find

$$I(t_2)(1 - e^{-t_2}) = 2B(t_2)(1 - e^{-t_2}),$$

which is the equality required. Making use of this, we have from (11) and (12)

$$E(t_2) = I'(t_2) = -E(0). \quad . \quad . \quad . \quad (14)$$

Now  $I'$  is essentially positive. Hence there is an excess of absorption over emission at the base and a numerically equal excess of emission over absorption at the top. This is the result stated. The excess can only be zero if  $I'(t_2)$  is zero, *i. e.* if  $t_2$  is zero.

It should be noticed that the departure from radiative equilibrium at the base and at the top is very appreciable. The ratio of the excess,  $2\pi k\rho dv E(t_2)$ , to the emission,  $4\pi k\rho dv B(t_2)$ , has the value

$$\frac{1}{2}(1 - e^{-t_2}); \quad . \quad . \quad . \quad . \quad (15)$$

if  $t_2 = 1.0$  this is 0.32, and if  $t_2 = 0.56$  it is 0.22; and it can be shown from Gold's data that these limits for  $t_2$  correspond to widely separated values of  $t_1$ , the total absorbing power of the atmosphere. Again,  $E(t)$  is a continuous function of  $t$ ; and hence, since it is positive when  $t = t_2$ , it will be positive in the upper parts of the convective atmosphere, violating the condition for convection. As we approach the earth it decreases, soon becoming negative, showing that in the lower portions the condition is satisfied.

We have assumed the atmosphere "grey" as regards the low-temperature radiation, and we have ignored the direct absorption of solar radiation. But a variation of the coefficient of absorption with wave-length does not affect the gist of the argument; a strictly isothermal upper atmosphere would still be an impossibility unless its optical

thickness were zero. As regards the solar radiation, Gold made an allowance for this by choosing  $\tau_2$  so that the left-hand side of (4) was slightly negative; but again the argument is unaffected. It appears then that Gold's analysis, though doubtless giving the broad outlines of the phenomenon, is inadequate in its details.

§ 3. Now the complete phenomenon must be very complex. Complications arise from the rotation of the earth, the change of insolation with latitude, cloud-structure, scattering, and the light from the sky, besides probably the world-wide circulation of the air; and the suddenness of the upper inversion has always been to some extent a difficulty. Instead of attempting to take account of the various influencing causes simultaneously, it would appear to be more in accordance with scientific method to construct a number of idealized models, to work out the theoretical solution for each separately, and then to examine the extent to which the earth's atmosphere partakes of their several characteristics.

§ 4. *The problem in principle.*—As a contribution towards this, it is proposed in this paper to consider the theory of the radiative equilibrium of a mass of absorbing and radiating material subject to insolation. The material is supposed to be stratified in parallel planes, and to be subject at its outer boundary to a parallel beam of incident radiation. The latter will be supposed in the first instance to be normal to the surface; later we shall examine the effect of oblique incidence. The material will be taken in the first instance to be grey; but later we shall suppose that there may be one coefficient of absorption for the incident radiation, another coefficient for the low-temperature radiation emitted by the material itself. Further, we shall assume the material to be infinitely thick, and to be in radiative equilibrium throughout its mass. The assumption of infinite thickness involves little or no loss of generality; we could, if we liked, consider a mass of finite thickness with an inner boundary consisting of a black radiating surface, but since our results will only involve the optical thickness, we need only suppose the absorption coefficient or the density to become suddenly very large at an assigned depth in order to deduce the case of an inner boundary from the solution for an infinitely thick slab of material.

The material being in a steady state must emit energy at its outer boundary equal to the incident radiation. Across

any plane parallel to the surface there will be a net outward flux of radiation derived from the material just balancing the inward flux of the residual solar radiation. In the far interior the latter will be greatly attenuated, and consequently the outward flux there must be small too. We should expect, therefore, that the temperature gradient in the far interior would be small; and this proves to be the case. In fact, *not only is there a definite limiting temperature at the outer boundary, as in the Schwarzschild case, but there is also a definite limiting temperature in the far interior.* This is one of the most interesting characteristics of the model we are discussing.

Let  $\tau$  be the optical thickness measured from the outer boundary to any point;  $I, I'$  the outward and inward intensities at any point at angles  $\theta$  and  $\psi$  with the normal;  $B(\tau)$  the intensity of black radiation for the temperature at the point  $\tau$ ;  $\pi S$  the intensity of the parallel beam of incident solar radiation *defined as the energy incident per second per unit area normal to the beam.* Here  $I$  and  $I'$  are to refer only to radiation derived from the material. It must be noted that since we have assumed the solar radiation to constitute a parallel beam, the definition of its intensity is necessarily different from the standard definition for conically spreading pencils\*.

The residual solar intensity at any depth  $\tau$  is  $\pi S e^{-\tau}$ . The equations of transfer are

$$\cos \theta \frac{dI}{d\tau} = I - B, \quad . \quad . \quad . \quad . \quad (16)$$

$$\cos \psi \frac{dI'}{d\tau} = B - I'. \quad . \quad . \quad . \quad . \quad (17)$$

The amount of energy emitted by an element  $dv$  per second is  $4\pi k p B dv$ . That absorbed is

$$k p dv \left[ \int I d\omega + \int I' d\omega' \right],$$

together with

$$\pi S e^{-\tau} k p dv.$$

Hence the equation of radiative equilibrium is

$$\int_0^{\frac{1}{2}\pi} I(\tau) \sin \theta d\theta + \int_0^{\frac{1}{2}\pi} I'(\tau) \sin \psi d\psi + \frac{1}{2} S e^{-\tau} = 2B(\tau). \quad (18)$$

The flux relation follows from (16), (17), (18), namely,

$$\int_0^{\frac{1}{2}\pi} I(\tau) \sin \theta \cos \theta d\theta - \int_0^{\frac{1}{2}\pi} I'(\tau) \sin \psi \cos \psi d\psi = \frac{1}{2} S e^{-\tau}. \quad (19)$$

\* See Planck, *Wärmestrahlung*, p. 15 (3rd edition).

From (16) and (17), with the appropriate boundary conditions,

$$I(\tau) = e^{\tau \sec \theta} \int_{\tau}^{\infty} B(t) e^{-t \sec \theta} \sec \theta dt, \quad . \quad . \quad (20)$$

$$I'(\tau) = e^{-\tau \sec \psi} \int_0^{\tau} B(t) e^{t \sec \psi} \sec \psi dt. \quad . \quad . \quad (21)$$

Substitute these in (18); write  $t = \tau + y \cos \theta$  in the first integral,  $t = \tau - y \sec \psi$  in the second, and replace  $\cos \theta$  and  $\cos \psi$  by  $\mu$ . We find

$$\begin{aligned} & \int_0^1 d\mu \int_0^{\infty} B(\tau + y\mu) e^{-y} dy \\ & + \int_0^1 d\mu \int_0^{\tau/\mu} B(\tau - y/\mu) e^{-y} dy + \frac{1}{2} S e^{-\tau} = 2B(\tau). \end{aligned}$$

We can now reverse the order of integration in the repeated integrals\*. Setting

$$C(\tau) = \int_0^{\tau} B(\tau) d\tau, \quad C'(\tau) = B(\tau),$$

we find finally for the integral equation for the temperature distribution,

$$\begin{aligned} C'(\tau) = \frac{1}{4} S e^{-\tau} & + \int_0^{\tau} \frac{C(\tau + y) - C(\tau - y)}{2y} e^{-y} dy \\ & + \int_{\tau}^{\infty} \frac{C(\tau + y)}{2y} e^{-y} dy. \quad . \quad . \quad . \quad (22) \end{aligned}$$

If we invert the orders of integration before making the substitutions for  $t$ , we obtain another form,

$$B(\tau) = \frac{1}{2} \int_0^{\infty} B(t) Ei(|t - \tau|) + \frac{1}{4} S e^{-\tau}, \quad . \quad . \quad (23)$$

which is the standard form for integral equations†.

Solutions of these may be sought directly. For an

\* For details, cf. Monthly Notices, lxxxi. p. 365 (1921).

† In equation (23)  $Ei$  denotes the exponential-integral function. The integral equation in the form (23) is substantially equivalent to the integral equation obtained by L. V. King in the analogous problem for scattering (Phil. Trans. 212 A. p. 375, 1912); it bears the same relation to King's equation that the author's integral equation for the atmosphere of a star in radiative equilibrium (M. N. lxxxix. p. 373, 1921) bears to Schwarzschild's integral equation for scattering in a stellar atmosphere (*Berlin Sitz.* 1914. p. 1183). But the form (22) is more convenient when solutions are being sought by successive approximation, and for other purposes.

approximate solution, however, it is quicker to employ the approximate forms of equations (16) to (19), obtained in the usual way. These are

$$\frac{1}{2} \frac{dI}{d\tau} = I - B, \quad \frac{1}{2} \frac{dI'}{d\tau} = B - I', \quad . \quad . \quad (24), (25)$$

$$I + I' + \frac{1}{2} S e^{-\tau} = 2B, \quad . \quad . \quad . \quad (26)$$

$$I - I' = S e^{-\tau}. \quad . \quad . \quad . \quad (27)$$

From the two latter,

$$I = B + \frac{1}{4} S e^{-\tau},$$

$$I' = B - \frac{3}{4} S e^{-\tau},$$

But  $I'(0) = 0$ . Consequently  $B_0 = \frac{3}{4} S$ . Inserting this approximate value of  $I$  in (24), we find

$$\frac{dB}{d\tau} = \frac{3}{4} S e^{-\tau},$$

whence, using the value of  $B_0$  already found,

$$B(\tau) = \frac{3}{2} S (1 - \frac{1}{2} e^{-\tau}). \quad . \quad . \quad . \quad (28)$$

It follows that there is a limiting temperature in the far interior, given by  $B_\infty = \frac{3}{2} S$ . If now  $T_0$  is the boundary temperature,  $T_1$  the effective temperature of the whole mass viewed from the outside,  $T_\infty$  the temperature in the far interior, and  $\sigma$  Stefan's constant, we have

$$\sigma T_0^4 = \pi B_0 = \frac{3}{4} \pi S,$$

$$\sigma T_\infty^4 = \pi B_\infty = \frac{3}{2} \pi S,$$

$$\sigma T_1^4 = \pi S,$$

and thus

$$T_\infty^4 : T_1^4 : T_0^4 = \frac{3}{2} : 1 : \frac{3}{4}. \quad . \quad . \quad . \quad (29)$$

It is important to notice that  $T_\infty$  is different from  $T_1$ , contrary to what might have been anticipated; also that the relation between  $T_1$  and  $T_0$  is different from that in the Schwarzschild case, where the net flux is the same at all depths. Notice also  $T_\infty^4 = 2T_0^4$ .

These values and the general distribution of temperature given by (28) are only approximations. To test them, let us re-employ (28) in (20) to obtain  $I$  and so check the radiative equilibrium at the boundary and the net flux



there. We find

$$I(\tau, \theta) = \frac{3}{2}S \left( 1 - \frac{\frac{1}{2}e^{-\tau}}{1 + \cos \theta} \right),$$

whence

$$I(0, \theta) = \frac{3}{2}S \frac{\frac{1}{2} + \cos \theta}{1 + \cos \theta}. \quad \dots \quad (30)$$

This gives the distribution of the emergent radiation—the law of bolometric darkening. Inserting in (18), the total absorption near the boundary is found to be proportional to  $(2 - \frac{3}{4} \log 2)S$ , the emission to  $\frac{3}{2}S$ —*i. e.* 0·987 instead of unity, an error of only 1·3 per cent. Again, from (19), the net flux at the boundary is given as  $(\frac{3}{2} \log 2)\pi S$  instead of  $\pi S$ —*i. e.* 1·040 instead of unity, an error of 4·1 per cent. The smallness of these discrepancies shows that (28) and the values (29) are satisfactory approximations.

To obtain a better approximation, knowing now something of the form of  $B$  from (28), we can assume

$$B(\tau) = a - be^{-\tau}$$

and choose  $a$  and  $b$  so that the correct net flux is given at the boundary and the condition of radiative equilibrium is satisfied there. It is found that the condition of radiative equilibrium in the far interior is then automatically satisfied, save for terms which tend to zero. We find

$$I(0, \theta) = a - \frac{b}{1 + \cos \theta},$$

whence from (18) and (19)

$$a - b(2 - \log 2) = \frac{1}{2}S,$$

$$\frac{1}{2}a - b(1 - \log 2) = \frac{1}{2}S.$$

These give

$$a = S/\log 2 = 1·4427 S,$$

$$b = \frac{1}{2}S/\log 2 = 0·7213 S;$$

whence  $B_0 = 0·7213 S$ ,  $B_\infty = 1·4427 S$ , and

$$T_\infty^4 : T_1^4 : T_0^4 = 1·443 : 1 : 0·721.$$

Thus the values of  $T_\infty$  and  $T_0$  in terms of  $T_1$  come out about 1 per cent. smaller than on the previous approximation. The relation  $T_\infty^4 = 2T_0^4$  still holds. The change is so trifling that we shall not attempt to obtain further approximations, which can be sought by using the integral equation. We shall

content ourselves with observing that in the exact solution the differential coefficient  $B'(\tau)$  has a singularity at  $\tau=0$ , becoming infinite \* like  $\log \tau$ . This is easily proved.

§ 5. *Extension to non-grey absorption.*—Let us now suppose that the material has a different coefficient of absorption for the incident radiation, say equal to  $n$  times that for its own low temperature radiation;  $n$  will usually be a small fraction. The inward solar intensity at  $\tau$  is now  $Se^{-n\tau}$ . Hence in the flux equation, (19),  $e^{-\tau}$  must be replaced by  $e^{-n\tau}$ , and in the equation of radiative equilibrium, (18),  $Se^{-\tau}$  must be replaced by  $nSe^{-n\tau}$ . Proceeding as before, we find that

$$B(\tau) = S \frac{1 + \frac{1}{2}n}{n} [1 - (1 - \frac{1}{2}n)e^{-n\tau}], \quad . \quad . \quad (28')$$

$$B_{\infty} = S \frac{1 + \frac{1}{2}n}{n}, \quad B_0 = \frac{1}{2}S(1 + \frac{1}{2}n),$$

$$T_{\infty}^4 : T_1^4 : T_0^4 = \frac{1}{2} + n^{-1} : 1 : \frac{1}{2}(1 + \frac{1}{2}n). \quad . \quad (29')$$

As  $n \rightarrow 0$ ,  $T_{\infty} \rightarrow \infty$ ,  $T_0^4 \rightarrow \frac{1}{2}T_1^4$ , and the temperature distribution tends to

$$B(\tau) = S(\frac{1}{2} + \tau).$$

The limiting case is, in fact, the Schwarzschild case for a constant net flux  $\pi F$ . Notice that  $T_{\infty}^4 = 2T_0^4/n$ .

§ 6. *Extension to oblique incident radiation.*—Next suppose that the external radiation is incident at an angle  $\alpha$  with the normal. If we preserve the same intrinsic intensity, the amount incident per unit area is now  $S \cos \alpha$  and the amount crossing unit area at depth  $\tau$  is  $S \cos \alpha e^{-n\tau \sec \alpha}$ . We can obtain the solution by putting  $S \cos \alpha$  for  $S$  and  $n \sec \alpha$  for  $n$  in the foregoing formulæ. We find

$$B(\tau) = S \frac{\cos \alpha + \frac{1}{2}n}{n} [\cos \alpha - (\cos \alpha - \frac{1}{2}n)e^{-n\tau \sec \alpha}], \quad (28'')$$

$$B_{\infty} = S \cos \alpha (\cos \alpha + \frac{1}{2}n)/n, \quad B_0 = \frac{1}{2}S(\cos \alpha + \frac{1}{2}n),$$

$$\begin{aligned} T_{\infty}^4 : T_1^4 : T_0^4 &= \cos \alpha (\frac{1}{2} + n^{-1} \cos \alpha) : \cos \alpha : \frac{1}{2}(\cos \alpha + \frac{1}{2}n) \\ &= \frac{1}{2} + n^{-1} \cos \alpha : 1 : \frac{1}{2}(1 + \frac{1}{2}n \sec \alpha). \quad . \quad (29'') \end{aligned}$$

Notice that  $T_{\infty}^4 = 2 \cos \alpha T_0^4/n$ .

\* Cf. Monthly Notices, lxxxi. p. 367 (1921).

§ 7. These formulæ offer several points of interest. As  $\alpha$  increases from 0 to  $\frac{1}{2}\pi$  and  $\cos \alpha \rightarrow 0$ ,  $T_0$  tends to a definite non-zero limit, although  $T_1$  tends to zero;  $T_0$  steadily decreases as  $\alpha$  increases, the limit being given by  $\sigma T_0^4 = \frac{1}{4}\pi nS$ ;  $T_x$  tends to zero. It appears, then, that for sufficiently oblique incidence the boundary is warmer than the interior. Consider now the temperature distribution given by (28'). When  $\cos \alpha = \frac{1}{2}n$ ,  $B(\tau)$  is constant and equal to  $\frac{1}{2}nS$  or  $S \cos \alpha$ , and the state is isothermal everywhere; and when  $\cos \alpha < \frac{1}{2}n$ , the temperature steadily decreases inwards in the interior. In spite of this there is at each point a net flux in the outward direction; so that here we have a case where the net flux is in the opposite direction to the temperature gradient. This would seem to be a novelty in the theory of radiative equilibrium. (It is easy to assure one's self that no contradiction with the second law is involved.) These results are based only on the approximate formulæ (28'') and (29''), but further investigation confirms them. It is easy to see in a general way how these curious temperature distributions arise. When the solar radiation is nearly tangential, its effective intensity is very weak, but owing to its obliquity it is entirely absorbed in a thin layer close to the surface (provided  $n$  is not zero). This layer is enabled to assume a definite temperature, but no residual radiation penetrates to the interior, which remains near the absolute zero. The outward net flux is maintained at any point in virtue of the outward radiation from the large amount of cold material inside the point overpowering the inward radiation from the small amount of warm material outside it. In the limit when  $\alpha = \frac{1}{2}\pi$ , the distribution of temperature is discontinuous; the temperature is zero everywhere, except at points in the surface.

§ 8. *Effect of rotation.*—These results can only be applied to a thick spherical atmosphere on the assumption that the solar energy incident on any one place is all re-radiated from that same place. Making this assumption, let us tentatively take into account the effects of rotation. We will calculate the time mean of the temperatures in any given latitude  $\lambda$  on the assumption that the axis of rotation is perpendicular to the ecliptic. If  $\phi$  is the hour-angle of the sun, its zenith distance  $\alpha$  is given by  $\cos \alpha = \cos \phi \cos \lambda$ . Taking (29'') as giving the "instantaneous" temperature during the day and taking the latter as zero during

the night, and using bars to denote mean values, we have

$$\begin{aligned}\frac{\sigma}{\pi} \overline{T_0^4} &= \overline{B_0} = \frac{1}{\pi} \int_0^{\frac{1}{2}\pi} B_0 d\phi = S \frac{\frac{1}{2}(\cos \lambda + \frac{1}{4}n\pi)}{\pi}, \\ \frac{\sigma}{\pi} \overline{T_1^4} &= \overline{B_1} = \frac{1}{\pi} \int_0^{\frac{1}{2}\pi} S \cos \lambda \cos \phi d\phi = S \frac{\cos \lambda}{\pi}, \\ \frac{\sigma}{\pi} \overline{T_\infty^4} &= \overline{B_\infty} = \frac{1}{\pi} \int_0^{\frac{1}{2}\pi} B_\infty d\phi = S \frac{\frac{1}{2} \cos \lambda (1 + \frac{1}{2}n^{-1} \pi \cos \lambda)}{\pi}.\end{aligned}\quad . . . (31)$$

When this averaging is taken into account, the approximately isothermal state ( $T_\infty = T_0$ ) is found to occur for  $\cos \lambda = n/\sqrt{2}$ ; for this value of  $\lambda$ ,

$$\overline{T_0^4}/\overline{T_1^4} = \frac{1}{2}(1 + \frac{1}{4}\pi\sqrt{2}) = 1.055,$$

which is sufficiently near unity. The general run of the change of temperature distribution with latitude has the same features as before.

§ 9. *Comparison with Emden.*—The formal problems discussed by Emden in the paper already mentioned and his method of solution are very similar to those discussed above, except that he takes the material to be bounded below by a black surface. Emden considers the radiative equilibrium of an atmosphere subject to external solar radiation in two cases: (1) the case of "grey radiation," by which he means the case in which the mean coefficient of absorption for the solar radiation is equal to that for the atmospheric radiation; this is the case  $n=1$  above; (2) the case in which the radiation spectrum can be divided into two ranges which have different mean coefficients of absorption, the solar radiation being entirely confined to one of them; this is practically our general case in which  $n$  is not unity. In each case he considers the solar radiation to be "gleichmässig verteilt," *i. e.* not as being confined to a parallel beam, but as uniformly distributed over the solid angle  $2\pi$ ; consequently he does not consider the variation of the state of equilibrium with latitude. The two main results to which he draws attention are: in case (1) the whole atmosphere must be isothermal, at a temperature equal to the "effective" temperature  $T_1$  calculated from the incident radiation with allowance for the albedo (see p. 873 above); in case (2) the state is not isothermal and the boundary temperature  $T_0$  is connected with the effective temperature

$T_1$  by the relation

$$T_0 = T_1 \left[ \frac{1}{2} (1 + k_1/k_2) \right]^{\frac{1}{2}}, \quad \dots \quad (32)$$

where  $k_1$  and  $k_2$  are the coefficients of absorption for the solar and terrestrial radiations.

Both these results are in apparent contradiction with those obtained in this paper. The source of the discrepancies is in each case Emden's assumption that the incident radiation may be taken to be diffuse. The way this occurs is as follows:—The mean coefficient of absorption for diffuse radiation incident on a thin layer of material is approximately twice the coefficient of absorption for a parallel beam incident normally, *i. e.* twice the coefficient of absorption as ordinarily defined. This fact allows us to approximate to the equations of transfer (equations (1) and (2) above) by replacing them by the "equations of linear flow"; in equations (5) and (6) we have explicitly adopted a new optical thickness  $t$  equal to twice the optical thickness  $\tau$  obtained directly from the ordinary coefficient of absorption; in equations (24) and (25) we have retained the optical thickness  $\tau$  and simply replaced the factors  $\cos \theta$  and  $\cos \psi$  by the value  $\frac{1}{2}$ ; the result is the same as if all the diffuse radiation were supposed to be confined to beams at an angle of incidence of  $60^\circ$  with the planes of stratification. Emden approximates in the same way as we have done, but since he takes the solar radiation to be diffuse he is adopting for this also a coefficient of absorption twice the value for a permanent beam. His results may therefore be expected to agree with ours if in ours we put  $\cos \alpha = \frac{1}{2}$ ,  $\alpha = 60^\circ$ ; and this in fact they do. But they lose part of their significance. His result for case (1) is of course true for diffuse radiation; indeed it is obvious thermodynamically, without proof, that material exposed to *isotropic* incident radiation will, if in radiative equilibrium, take up a temperature equal to that of the radiation: the case is practically that of a black body enclosure. But our results show that if the incident radiation occurs *as a parallel beam*—as, in fact, solar radiation does—then the isothermal state is merely the particular distribution of temperature that happens to correspond to an angle of incidence of  $60^\circ$ . Further, Emden's result does not suggest another of our results—that when  $n \neq 1$  there also exists an isothermal state of equilibrium: namely, for  $\cos \alpha = \frac{1}{2}n$  for a fixed parallel beam, and for  $\cos \lambda = n/\sqrt{2}$  when rotation is taken into account. Emden's formula (32)



above should be compared with our formula for a fixed beam incident at  $\alpha$  (from (29'')),

$$T_0 = T_1 \left[ \frac{1}{2} \left( 1 + \frac{1}{2} n \sec \alpha \right) \right]^{\frac{1}{4}}, \quad . \quad . \quad . \quad (33)$$

where  $n = k_1/k_2$ ; and with the rotational mean formula (from (31)),

$$T_0 = T_1 \left[ \frac{1}{2} \left( 1 + \frac{1}{4} n \pi \sec \lambda \right) \right]^{\frac{1}{4}}, \quad . \quad . \quad . \quad (34)$$

Emden's formula differs but little from the latter when  $\lambda = 0$ , as is to be expected.

Emden does not obtain the integral equation for the temperature distribution. For the sake of completeness it seems worth putting on record the integral equation for the general case involving  $n$  and  $\alpha$ . It is deduced in the same way as (22) :—

$$\begin{aligned} C'(\tau) = \frac{1}{4} n S e^{-n\tau \sec \alpha} + \int_0^\tau \frac{C(\tau + y) - C(\tau - y)}{2y} e^{-y} dy \\ + \int_\tau^\infty \frac{C(\tau + y)}{2y} e^{-y} dy. \quad . \quad . \quad (35) \end{aligned}$$

§ 10. *Effect of an internal boundary.*—We shall next consider the case in which the material is bounded internally by a black surface at  $\tau = \tau_1$  instead of extending to infinity. It has already been mentioned that as the formulae only involve the optical thickness  $\tau$ , we may deduce the results for this case by supposing that immediately beneath  $\tau = \tau_1$  the density suddenly increases indefinitely. The temperature distribution above  $\tau_1$  is unaltered. It might at first be supposed that the black surface would assume a temperature equal to  $T_\infty$ , but this is not so. For the infinite density gradient we have postulated at the level  $\tau_1$  implies an infinite radiation gradient there, and (unless we are prepared to accept the existence of an infinite temperature gradient at the black surface) the surface will take up a temperature intermediate between  $T(\tau_1)$ , the temperature of the material in contact with the surface, and  $T_\infty$ . This temperature, say  $T_s$ , is easily calculated. For since the surface must re-radiate all the radiation falling on it, we shall have  $\sigma T_s^4 = \pi B_s$ , where  $B_s$  is given by

$$B_s = I'(\tau_1) + S \cos \alpha e^{-n\tau_1 \sec \alpha} \quad . \quad . \quad (36)$$

From the equations

$$I + I' + \frac{1}{2}nS e^{-n\tau \sec \alpha} = 2B, \quad \dots \quad (26'')$$

$$I - I' = S \cos \alpha e^{-n\tau \sec \alpha}, \quad \dots \quad (27'')$$

we find

$$I' = B - \frac{1}{2}S e^{-n\tau \sec \alpha} (\cos \alpha + \frac{1}{2}n).$$

Hence

$$B_s = B(\tau_1) + \frac{1}{2}S(\cos \alpha - \frac{1}{2}n)e^{-n\tau_1 \sec \alpha}. \quad \dots \quad (37)$$

If  $\cos \alpha > \frac{1}{2}n$ , which will usually be the case in applications,  $B_s$  is greater than  $B(\tau_1)$ . Thus the temperature of the surface exceeds that of the material (say air) in contact with it. Hence convection currents would be set up, and the state of radiative equilibrium would be destroyed. This is a simple way of demonstrating the impossibility of the existence of a state of radiative equilibrium throughout the entire atmosphere.

§ 11. *The "greenhouse" effect.*—Inserting in (27) the value of  $B(\tau_1)$  from (28''), we have

$$B_s = S \cos \alpha [(\cos \alpha + \frac{1}{2}n) - (\cos \alpha - \frac{1}{2}n)e^{-n\tau_1 \sec \alpha}]/n. \quad (38)$$

Now if the black surface were exposed to the direct insolation  $\pi S \cos \alpha$ , without the intervention of an atmosphere, it would take up a temperature  $T_s'$  given by

$$\sigma T_s'^4/\pi = B_s' = S \cos \alpha.$$

Hence

$$\frac{T_s^4}{T_s'^4} = 1 + \frac{(\cos \alpha - \frac{1}{2}n)(1 - e^{-n\tau_1 \sec \alpha})}{n}. \quad \dots \quad (39)$$

Thus, when  $\cos \alpha > \frac{1}{2}n$ , the surface is maintained at a temperature higher than it would be in the absence of an atmosphere. The ratio  $T_s^4/T_s'^4$  increases as  $n$  decreases, the limit as  $n \rightarrow 0$  being  $1 + \tau_1$ . The case of diffuse incident radiation is roughly given by putting  $\cos \alpha = \frac{1}{2}$ , and then the condition is  $n < 1$ , i. e. that the atmosphere or "protecting layer" must be more transparent to the incident radiation than to the radiation returned. This is the radiation part of the "greenhouse" or "heat-trap" effect, which is sometimes the subject of fallacious statements; it must of course be distinguished from that part of the effect which is due to the prevention of convection.

§ 12. *Extension to a partially convective atmosphere.*—We will now generalize the problem a little further. Suppose that we have a state of affairs in which the material above a

given level  $\tau = \tau_2$  is in strict radiative equilibrium, that below the given level merely in radiative equilibrium *as a whole*; below  $\tau = \tau_2$  the temperature distribution may be of any form (with or without a lower bounding surface) subject only to the condition that the whole system below  $\tau_2$  radiates outwards as much as it absorbs; in general, convection of heat will be required in the region below  $\tau = \tau_2$  in order to maintain a steady state. Then it is easily seen that the temperature distribution above  $\tau_2$  is exactly the same as if the lower region were in radiative equilibrium in the strict sense; for the upward intensity at  $\tau_2$ , namely  $I(\tau_2)$ , is the same in the two cases. Hence the temperature distribution we have already found applies to the region above  $\tau_2$ . The importance of this point from the point of view of applications to the earth's troposphere and stratosphere is evident\*.

§ 13. *The boundary between troposphere and stratosphere.*—It is convenient to denote the regions below and above the level  $\tau_2$  in our ideal problem by the words "troposphere" and "stratosphere" respectively, without implying any reference to these actual regions in the earth's atmosphere. Then § 12 shows that under the conditions there stated a stratosphere cannot be isothermal unless its optical thickness is zero or  $\cos \alpha = \frac{1}{2}n$ . If the optical thickness is not zero and  $\cos \alpha > \frac{1}{2}n$ , the lower parts of the stratosphere must be warmer than the upper. This agrees with § 2, where it was found that Gold's stratosphere is warming up at the base.

We are now in a position to frame in a precise manner the problem of where the division between troposphere and stratosphere should occur, in the ideal case. Let us suppose that there is a certain distribution of temperature which the processes of convection tend to set up throughout the whole atmosphere. Let the corresponding black body radiation-function be expressed as a function of optical depth, say  $B_e(\tau)$ . This temperature distribution together with the lower boundary surface implies a definite upward intensity of radiation at any point  $\tau$ , say  $I_e(\tau)$ , which is determinate and calculable when  $B_e(\tau)$  is given. Let  $\tau_2$  denote the optical depth of the surface of separation between troposphere and stratosphere which it is required to determine. Then

\* The points which are the subject of §§ 10, 11, 12 are substantially made by Emden, in the form appropriate to diffuse radiation. But Emden's analysis is in parts a little complicated by his introducing unnecessarily early into the investigation an empirical expression for the water-vapour in the earth's atmosphere as a function of height.

below  $\tau_2$  the temperature is given by  $B_c(\tau)$ ; above  $\tau_2$  it is given by the function  $B(\tau)$  given by formula (28''). At  $\tau_2$  the upward intensity of radiation is that appropriate to the state of radiative equilibrium; it is the value  $I(\tau_2)$  deducible from (26'') and (27''),

$$I(\tau_2) = B(\tau_2) + \frac{1}{2}S(\cos \alpha - \frac{1}{2}n)e^{-n\tau_2 \sec \alpha}.$$

*Hence  $\tau_2$  is the root of the equation*

$$I_c(\tau_2) = I(\tau_2). \quad . \quad . \quad . \quad . \quad (40)$$

Suppose this equation is solved. *It by no means follows that*

$$B_c(\tau_2) = B(\tau_2);$$

i. e. *it by no means follows that the temperature immediately below the junction is continuous with that immediately above it.* Further, even if it happens that these temperatures are equal, it does not follow that the condition for a convective atmosphere is satisfied in the region immediately below  $\tau_2$ . For a physically possible distribution both these conditions must be satisfied. Hence, in general, it is not possible to determine a level  $\tau_2$  such that a *prescribed* temperature distribution exists up to  $\tau_2$  and a radiative one above it.

The question must therefore be studied in the reverse order: what conditions does the existence of a stratosphere of non-zero optical thickness impose on the temperature distribution in the upper troposphere? It would make the present paper too long to take up the investigation here. But it appears to be possible to show that if the temperature is continuous at  $\tau_2$ , then *in general* (but not necessarily) the temperature gradient is discontinuous there. This is, of course, what is observed.

In the earth's stratosphere, on the other hand, the observed absence of vertical gradients strongly suggests that if it is in strict radiative equilibrium its optical thickness is practically zero. For the particular relation ( $\cos \alpha = \frac{1}{2}n$  or  $\cos \lambda = n'\sqrt{2}$ ) which is necessary for an isothermal stratosphere of non-zero optical thickness cannot be satisfied save in very high latitudes; and even here (as we shall see) this would be prevented by the additional radiation due to world-wide convection. Further, we have seen in § 2 that if the absorption of solar radiation is neglected, an isothermal stratosphere would soon cease to be isothermal and would be disturbed by convection currents. If now the optical thickness of the stratosphere is practically zero, a state of radiative equilibrium will probably extend a little way below the tropopause, and the observed suddenness of the demarcation must

be due to a sudden diminution of absorbing power. This, again, would indicate the tropopause as the boundary of the water-vapour atmosphere. The contrary has, however, been urged by Gold \* on different grounds, and it is difficult to deny the force of his arguments. The matter is obviously one of considerable difficulty.

14. *Applications.*—This concludes the discussion of the idealized problem of which it is the main business of the paper to give an account. The theory is capable of a number of applications to the earth's atmosphere, but the principal of these, at least in the case when the incident radiation may on the average be taken to be diffuse, have already been made by Emden. Perhaps the result most directly useful is the correction to the Schwarzschild boundary temperature due to the absorption of the incident radiation there, given by formulæ (33) or (34), or Emden's form (32). (The Schwarzschild temperature is given by putting  $n=0$ .) From a discussion of the observational material, Emden finds that  $n$  may be taken to be  $\frac{1}{23}$ . With  $\cos \alpha = \frac{1}{2}$  this gives an increase of 1 per cent., making the calculated value of  $T_0$  (see § 1) about  $216^\circ$ . If  $n$  is taken equal to  $\frac{1}{10}$ ,  $T_0$  becomes  $219^\circ$ , the observed value.

Another application made by Emden is to show that an atmosphere entirely in radiative equilibrium would be an impossibility, even in the absence of the warming effect due to the earth's surface (§ 10 above). For, taking into account the water-vapour distribution, radiative equilibrium implies at a sufficient depth temperature gradients in excess of the critical gradient for stability; so that convection currents would be set up. Emden finds that this would occur at a height of about 3 km.

When Emden wrote, the variation of the temperature of the stratosphere and height of the tropopause with latitude was not fully appreciated. And in the light of this variation, the small improvement in agreement, due to the introduction of  $n$ , between the Schwarzschild temperature and the observed mean temperature for S.E. England becomes largely meaningless. What is astonishing, *a priori*, is that the two temperatures should agree as well as they do. The agreement can only mean that the *actual* temperature of the stratosphere over S.E. England must be very close to the *mean* temperature over the earth. The agreement is partly helped by the circumstance that the latitude of England is

\* Geophysical Memoirs, No. 5, p. 129 (1913).



close to  $60^\circ$ ; and we have seen that the value  $\alpha = 60^\circ$  plays a special part in the theory.

It is therefore interesting to inquire whether the theory developed in the present paper has any bearing on the question of the origin of the variation with latitude. The facts to explain are that the temperature of the stratosphere increases as the latitude increases, and that the height of the tropopause decreases. Reference to recent books on meteorology and the physics of the air shows that there is no accepted detailed explanation.

Assuming that a stratosphere is optically very thin, it will be very nearly isothermal and its temperature will be equal to  $T_0$ . Formula (34) shows at once that the ratio of  $T_0$  to  $T_1$  (the effective temperature of the insolation) increases as  $\lambda$  increases, provided  $n$  is not zero, and that the increase becomes relatively large for high latitudes. As seen in § 7, this is due to the increased absorption of the solar radiation in the more superficial layers. This does not seem to have been suggested before, and it may in fact be one of the contributory causes of the increased temperature in higher latitudes. But the first of formulæ (31) shows that the actual value of  $T_0$  decreases as  $\lambda$  increases. All the theory indicates is that  $T_0$  decreases much more slowly than  $T_1$  as  $\lambda$  increases, and so the absolute increase of  $T_0$  as observed is not accounted for. The tendency to increase would be helped if it could be shown that  $n$  increased with  $\lambda$ , *i. e.* if the ratio of absorption of solar radiation to that of terrestrial radiation increased with latitude. Some effect of this kind there must be; for carbon dioxide is more important as an absorber of solar radiation than of terrestrial radiation, and owing to the decreased humidity in high latitudes the ratio of carbon dioxide to water vapour is there greater. But this, again, would not appear to be sufficient.

It must now be recalled that we have assumed throughout that any portion of the surface radiates away an amount of energy equal to that incident on it. But we know that this is not true for the earth's surface. Heat is convected from the equatorial regions toward the polar regions: otherwise the change of surface temperature with latitude would be much more severe than it is. Hence the equatorial regions must radiate less than they receive, the polar regions more. Now if  $\pi F$  is the additional net outward flux (positive or negative), the radiative distribution of temperature is obtained by adding the term  $F(\frac{1}{2} + \tau)$  to the right-hand of (28''), and the boundary temperature is given by

$$\sigma T_0^4 / \pi = \frac{1}{2} F + \frac{1}{2} S (\cos \alpha + \frac{1}{2} n). \quad . . . \quad (41)$$

A similar formula holds when rotation is taken into account. Since  $F$  is positive in high latitudes and negative in low,  $T_0$  should be greater in high latitudes and smaller in low than it would be in the absence of convection. Moreover, for some particular latitude  $F$  will be zero, and here the value of  $T_0$  will be the same as in the absence of world-wide convection. The agreement between calculation and observation for S.E. England thus implies that in this latitude the amount radiated is about equal to the solar radiation incident.

But  $T_0$  for high latitudes *exceeds* that for low. Now  $\pi(F + S \cos \alpha)$  is the total outward radiation to space. Hence (on the assumptions made) the total radiation to space in high latitudes must exceed that in low, unless the change of  $n$  is very considerable. This is a surprising result, but not necessarily impossible; if the stratospheric temperatures are really maintained to great heights under the influence of radiation there seems little escape from it. The difficulty is, of course, not new. Gold dealt with it as follows\*. Gold showed that if the absorbing power of the atmosphere increases, then the theoretical height of the tropopause increases. In the notation of § 2, it can be deduced from (4) that  $\tau_2$  though increasing with  $\tau_1$  is fairly insensitive to it. Roughly speaking, then, on Gold's theory the isothermal state sets in at a fixed optical depth below the outer boundary; hence the more absorbing the atmosphere the smaller is  $\tau_2/\tau_1$ , the smaller is  $p_2/p_1$ , and the greater is the height of the tropopause. The known increased humidity over the equator, with consequent increased absorbing power, would thus account for the observed increased height of the tropopause; and the lower temperature of the stratosphere follows from the increased height through which a convective gradient holds, even allowing for the higher ground temperature. But the above difficulty still remains, for the increased absorbing power implies a decreased outward radiation.

Gold argued from the improbability of this that "the atmosphere is not a 'grey' body, but must have nearly perfect transparency for some spectral region." It is well known that the coefficient of absorption varies considerably from place to place in the spectrum, whereas we have assumed it to possess but two values—one for solar radiation and one for terrestrial. But it is very doubtful whether this removes the difficulty. For there still has to be an equilibrium of radiation. One might reason generally that the transparency of the air in certain spectral regions

\* Geophysical Memoirs, i. p. 128 (1913).

would permit the escape of extra radiation which would have no effect in controlling the temperature. But the boundary temperature is not necessarily lower: it may be higher or lower, according to the spectral regions in which the air is not transparent. It has recently been shown by the author\* that if a thin layer of material is exposed on one side to black radiation of effective temperature  $T_1$  and is in radiative equilibrium, then it will take up a temperature  $T_0$  which is equal to  $2^{-\frac{1}{2}}T_1$  (the Schwarzschild value) when the material is grey, but which, whatever the optical properties of the material, will satisfy the inequalities

$$T_1 > T_0 > \frac{1}{2}T_1;$$

and that  $T_0$  will approximate to  $T_1$  if the material is transparent save in the extreme ultra-violet, to  $\frac{1}{2}T_1$  if transparent save in the extreme infra-red. (Here "ultra-violet" and "infra-red" must be interpreted as relative to the value of  $\lambda_{\max}$  corresponding to  $T_1$ .) If, for simplicity, we neglect the absorption of solar radiation, the theorem can be applied as it stands to the stratosphere. It shows that the temperature will be less than for uniform absorption only if the absorption occurs principally on the long wave-length side of  $\lambda_{\max}$ .—in this case about  $10\ \mu$ . But water-vapour is least opaque† to long wave-length radiation in the region  $7\ \mu$  to  $20\ \mu$ , more particularly in the region  $8\ \mu$  to  $12\ \mu$ . There is, indeed, important carbon-dioxide absorption‡ in the region  $13\ \mu$  to  $16\ \mu$ , but this is usually considered to be not large compared with the water-vapour absorption. Without a detailed numerical investigation it would be difficult to estimate the resultant effect; but if carbon-dioxide absorption is important near the equator, it should be more important in higher latitudes, and this would go against the argument. If a relation  $T_0 = \epsilon T_1$  holds above the equator in virtue of selective radiative equilibria, it ought to hold too in higher latitudes; for it is difficult to see why the atmosphere at 20 km. above the equator should be optically different from that in higher latitudes in the direction of being relatively more absorptive above the equator on the red side of  $\lambda_{\max}$ . Moreover, if we do modify the selective optical properties of the atmosphere from equator to pole, then Gold's explanation

\* "The Temperature in the Outer Atmosphere of a Star," *Monthly Notices R. A. S.* lxxii. p. 368 (1922). See also Fabry, *Astrophys. Journ.* xlv. p. 269 (1917).

† Abbot, *Annals Astrophys. Obs. Smithson. Inst.* ii. p. 167 (1908).

‡ See, for example, Humphreys, 'Physics of the Air,' p. 88, 1920.

of the change of height of the tropopause no longer holds, at least without further examination.

In view of these considerations, it seems on the whole tenable that the outward radiation from the equator is less than from higher latitudes, and that the variation of stratospheric temperature must be principally due to the general circulation of the air in the convective region. (The connexion between the variation of temperature of the stratosphere and the observed uniformity of pressure at 20 km. over the whole earth has been pointed out by W. H. Dines\*.) The higher upper-air temperatures of high latitudes may still be helped by the increased direct absorption there, in the way we have seen.

§ 15. *Summary.*—It is shown that if the atmosphere is divided into two shells—a lower one (the troposphere) in convective equilibrium, and an isothermal one (the stratosphere),—then the stratosphere cannot be in strict radiative equilibrium unless its optical thickness for low-temperature radiation is zero, even if it is in radiative equilibrium as a whole. The only exception is when the lower region is also in radiative equilibrium as a whole and when, in addition, a special relation ( $\cos \alpha = \frac{1}{2}n$ , or  $\cos \lambda = n/\sqrt{2}$  when rotation is allowed for) exists between the angle of incidence of the solar radiation and the ratio of the coefficients of absorption of solar and terrestrial radiation. The theory of atmospheres in radiative equilibrium subject to insolation is discussed in detail for various cases, including the dependence of the temperature distribution on the angle of incidence of the solar radiation. An integral equation for the temperature is obtained. Comparison is made with Emden's work. From an application of the results to the earth's atmosphere it is inferred that the variation of the temperature of the stratosphere with latitude cannot be accounted for on radiation principles unless the total radiation of the earth to space is greater in high latitudes than in low latitudes. This is probably the case, and the observed distribution of stratospheric temperature is probably connected with the general circulation of the air; however, the increased direct absorption of solar energy in the upper levels in high latitudes must have some effect.

It is intended to insist principally on the general theory, and the applications are only made tentatively.

July 17, 1922.

\* Geophysical Memoirs, No. 13, p. 71 (1919).



LXXV. *On the Molecular Theory of Solution. II.*

By S. C. BRADFORD, D.Sc.\*

IN a previous paper† a preliminary attempt was made to consider the phenomena of solution from the point of view of molecular energy and attractive forces. Recent advances in atomic theory make it fairly certain that atoms and molecules are surrounded by fields of force. Indeed it has long been recognized that cohesion and surface tension are due to molecular forces. But the part played by these forces in the phenomena of solution has not been considered sufficiently. We have to take into account the cohesion of the solvent, the adhesion of solvent and solute, and the cohesion of the solute. When a solid is brought into contact with a liquid, the surface tension of the solid, due to the unbalanced cohesive forces at its surface, is reduced by the counter attraction of the liquid particles for those of the solid. On this account an appreciable number of solid particles may have sufficient kinetic energy to overcome the diminished surface forces and escape into the liquid. But any that come again within the range of attraction of the solid surface will be reclaimed, so that eventually a statistical equilibrium may be attained when the numbers of particles leaving and returning to the solid are equal. This state, corresponding to the solubility of the solid, is determined by the equation

$$n_a = n_b e^{-\frac{s^2}{\alpha^2}}, \quad . . . . . (i)$$

where  $n_a$  and  $n_b$  are the numbers of particles in unit volume of liquid and solid respectively,  $\alpha$  is the most probable speed of the particles, and  $s$  is a velocity satisfying the condition that the momentum normal to the surface,  $\frac{1}{2}ms^2$ , of a particle of the solute is just sufficient to carry it through the surface layer. Similar reasoning applied to a cooling solution‡ shows that it will pass through a metastable stage, as the diminishing kinetic energy allows the aggregation of the particles, until they reach such a size that the force of gravity dominates their Brownian movement, the particles settle out of solution, and the statistical equilibrium is re-established. By the application of Perrin's formula

$$r = \sqrt[3]{\frac{RT}{N} \cdot \frac{\log \frac{n_1}{n_2}}{\frac{4}{3}\pi g(\rho_1 - \rho_2)(x_2 - x_1)}}$$

\* Communicated by the Author.

† Phil. Mag. vol. xxxviii. pp. 696-705 (1919).

‡ Biochem. J. vol. iv. pp. 553-555 (1921).



it was calculated that the radius of a gelatin particle just large enough to settle would be about  $0.06 \mu$ . This agreed approximately with the value found experimentally by the application of Stokes' law.

As a first approximation, the force between two particles was taken as

$$F = \frac{M_a \cdot M_b}{r_{ab}^4}, \quad . . . . . \quad (ii.)$$

$r_{ab}$  being the distance between their centres. From this it was deduced that the initial force to be overcome by a particle of solid escaping into pure solvent is proportional to

$$f = \frac{M_w^2}{r_{w^2}^4} - 2 \frac{M_w \cdot M_s}{r_{ws}^4} + \frac{M_s^2}{r_{s^2}^4}, \quad . . . . . \quad (iii.)$$

where the subscripts  $w$  and  $s$  refer to liquid and solid respectively. The smaller this force, the greater the solubility.

In the normal case, when the molecular cohesion of the solute is greater than that of the solvent, the last term of (iii.) will be the largest, and the force opposing solution will be greater as the cohesion of the solute increases. That is to say, the solubility of ordinary salts is smaller the greater their cohesion. When the cohesion of the solute is less than that of the solvent, as often happens with organic substances, the middle term of (iii), representing the adhesion of solute and solvent, will be greater than the last. In this case the solubility will increase with increasing adhesion of solute and solvent. And since the adhesion increases with the cohesion of the solute, the solubility of such substances is greater, the larger their cohesion. Similarly the solubility of a given solute, in different solvents with less cohesion, will increase with the cohesion of the solvent, while the solubility of the same solute, in solvents with greater cohesion, will diminish with increasing cohesion of the solvent.

Relative molecular cohesion may be estimated in a variety of ways. Traube\* used the enhanced or diminished surface tension of a solution as a measure of the adhesion of solute and solvent. He considered solubility only from the point of view of adhesion, but was able to show that the solubilities of organic liquids, which reduce the surface tension of water, follow the order of the surface tensions of their solutions. As, however, he neglected to take into account the mutual cohesions of both solvent and solute as well as their kinetic

\* *Ber. deut. chem. Ges.* vol. xlii. p. 86 (1906).

energy, he failed to explain why the solutions of many other substances, which increase the surface tension of water, decrease with increasing surface tension of their solutions. When all the factors are considered, as above, it is found that the solubilities of substances generally, whether solid, liquid, or gaseous, can be accounted for, and that when substances are arranged in the order of their solubilities they are in the order of every other property of solutions. It was pointed out that exceptions may be expected when the distances of the electric charges of the particles may be influenced by the configurations of the unlike particles, so that the adhesive forces may differ from those calculated from the respective cohesions according to formula (iii). In this way, however, the theory gives a picture of the processes of solution and crystallization, and indicates for the first time the cause of the widely differing solubilities and solvent powers of different substances.

On the assumption of molecular fields of force, it may be easy to understand why such properties of solutions as solubility, degree of hydration, heat of solution, molecular volume and compressibility, should follow the order of their surface tensions. But, at first sight, it may be surprising that the same should be true of the depression of the freezing-point, elevation of the boiling-point, vapour pressure, and electrical conductivity, with the suggestion that, were sufficient determinations available, osmotic pressure would be included. The inference can hardly be avoided that these properties, also, are influenced by the molecular fields. As with solubilities, Traube attempted, unsuccessfully, to account for the coincidence by considering only the adhesion of solute and solvent. That these properties are affected by the molecular attractions is, however, a direct result of the present theory.

A solution may be considered as a liquid in which a number of its ultimate particles have been replaced by others having the same average kinetic energy but exerting different fields of force. The concentration of solvent will be less and the internal pressure of the solution will differ from that of the solvent. Kleeman\* has shown that the intrinsic pressure of a solution is given by the relation

$$P_n = P_{nw^2} + 2P_{nws} + P_{ns^2},$$

where  $P_{nw^2}$  and  $P_{ns^2}$  are the attractions exerted, respectively, across a plane by the molecules of the kinds  $w$  and  $s$  on the molecules of the same kind in a cylinder of unit cross-section

\* 'A Kinetic Theory of Gases and Liquids,' p. 202 (1920).



this equation. More recently Kleeman \* deduced expressions for osmotic pressure in terms of molecular motion, attraction and volume, remarking that "it is evident . . . that osmotic pressure must arise through these properties of matter and the equations are therefore fundamental in character. They are, however, of little use in practice . . . since we have no means yet of determining experimentally how the quantities . . . vary."

Treatment of the problem was omitted from the preliminary paper in the hope of finding a more definite correlation. This was not far to seek. On account of the meagre, and sometimes doubtful, data available for osmotic pressure, cryoscopic determinations were considered. From the present point of view the depression of the freezing-point of a solution may be regarded as the sum of two effects: a normal depression corresponding to van't Hoff's formula

$$D = \frac{0.02T^2}{L}$$

due to the presence of a solute with the same molecular field as the solvent, together with an effect produced by the altered internal pressure of the solution. The molecular depressions of organic substances, having molecular fields not greatly different from that of the solvent, will not deviate much from the normal. But aqueous solutions of many salts show a marked increase in surface tension that indicates considerable alteration in internal pressure. The freezing-point depressions of such solutions should differ appreciably from the normal. Since both surface tension and intrinsic pressure are due to molecular attraction, we may take the one as proportional to the other. And since the freezing-point of water is depressed by increase of pressure, it follows that the freezing-points of aqueous solutions of salts should be greater than the normal by an amount which is proportional to the increase of surface tension. It must not be forgotten, however, that substances exhibiting greater molecular attraction than water may tend to aggregate in solution. This must happen at the higher concentrations. In this case the normal depression would be reduced correspondingly to the smaller number of solute particles. Moreover, the field of force surrounding the aggregated particles would differ from that round a simple particle and should be less on account of greater concentration of the lines of force within

\* *Loc. cit.*

the aggregate. These effects are the more likely with solutes having large molecular fields. Or again, as pointed out above, there may be a closer approximation of solute and solvent particles, on account of a suitable relation between the positions of the electric charges, with a corresponding alteration in the external field around the particles. Thus it is possible that a solute may reduce the surface tension of a solvent although the molecular field of the solute may be the greater. This effect is the more likely with solutes having hydroxyl or acidic hydrogen groups.

Such considerations do not increase the prospect of finding an exact ratio between the increments of surface tension and freezing-point depression. On this account the constancy in this ratio shown by the few substances for which there are data available is the more striking. In the table below, the observed depressions of the freezing-point are taken from Landolt and Börnstein's *Tabellen*, 1912. But as the determinations of surface tension were not made for the same concentrations as the freezing-point observations, the values given in the table were read from smooth curves drawn through points corresponding to the published figures, taking the surface tension of water as the zero point on each curve. On account of the sparseness of the observations there is a slight uncertainty in the values at the lower concentrations. More extensive determinations are desirable and are being undertaken.

The last column but one in the table shows the ratio between the increments in surface tension and depression of freezing-point, the normal depression being taken as  $1^{\circ}86$  per gram-mole per litre. The chlorides of barium, calcium, magnesium, and strontium behave like those of sodium or potassium. Copper and magnesium sulphates are the only other substances for which both cryoscopic data, and surface-tension determinations by the method of capillary rise, are available. Surface tensions observed by other methods do not correspond with the values obtained from the capillary rise, nor are they proportional to the increments in the depression of the freezing-point. The above-mentioned sulphates give depressions of freezing-point at moderate concentrations which are even less than the normal, so that it is clear that some disturbing factor, such as aggregation, comes into play.

With these two exceptions the constancy in the ratio is remarkable, being in many cases about 0.64. It is interesting to inquire the meaning of this figure. It has been assumed that the surface tension of a liquid is proportional to its



Grams 100 c.c.	g. moles litre.	Observed De- pression.	Normal De- pression.	Increase.	Surface Tension	Increase.	Ratio.	Increase of Surface Tension × 0.64.
Sodium Nitrate.								
0.43	0.05	0.17°	0.09°	0.08°	74.23	0.13	0.61	0.08
1.71	0.20	0.67	0.37	0.30	74.57	0.47	0.62	0.30
Potassium Nitrate.								
2.02	0.20	0.64°	0.37°	0.28°	74.52	0.42	0.64	0.27
2.53	0.25	0.77	0.47	0.30	74.57	0.47	0.65	0.30
5.06	0.50	1.47	0.93	0.54	74.86	0.76	0.73	0.49
7.59	0.75	2.11	1.40	0.71	75.04	0.94	0.75	0.60
10.12	1.00	2.66	1.86	0.80	75.22	1.12	0.71	0.72
Sodium Sulphate.								
1.42	0.10	0.43°	0.19°	0.24°	74.40*	0.30	0.80	0.19
2.84	0.20	0.81	0.37	0.44	74.74	0.64	0.69	0.41
4.27	0.30	1.16	0.56	0.60	75.06	0.96	0.62	0.61
7.11	0.50	1.84	0.93	0.91	75.69	1.59	0.57	1.01
Potassium Sulphate.								
0.87	0.05	0.23°	0.09°	0.14°	74.32	0.22	0.64	0.14
1.74	0.10	0.43	0.19	0.24	74.50	0.40	0.60	0.26
3.49	0.20	0.81	0.37	0.44	74.80	0.70	0.63	0.45
7.75	0.44	1.66	0.83	0.83	75.30	1.20	0.69	0.77
Sodium Carbonate.								
0.21	0.02	0.10°	0.04°	0.06°	74.19	0.09	0.69	0.06
0.53	0.05	0.23	0.09	0.14	74.32	0.22	0.63	0.14
1.06	0.10	0.44	0.19	0.25	74.50	0.40	0.64	0.26
2.12	0.20	0.83	0.37	0.46	74.83	0.73	0.63	0.47
5.31	0.50	1.88	0.93	0.95	75.57	1.47	0.65	0.94
Potassium Carbonate.								
0.14	0.01	0.05°	0.02°	0.03°	74.15	0.05	0.64	0.03
0.28	0.02	0.10	0.04	0.06	74.18	0.08	0.75	0.06
0.69	0.05	0.23	0.09	0.14	74.28	0.18	0.79	0.12
1.38	0.10	0.45	0.19	0.26	74.48	0.38	0.68	0.24
2.77	0.20	0.88	0.37	0.51	74.89	0.79	0.64	0.51
Sodium Chloride.								
0.63	0.11	0.38°	0.21°	0.17°	74.32	0.20	0.85	0.13
1.36	0.23	0.80	0.43	0.37	74.54	0.42	0.88	0.27
2.51	0.43	1.45	0.80	0.65	74.91	0.79	0.82	0.51
4.10	0.70	2.40	1.30	1.10	75.40	1.28	0.86	0.82
Potassium Chloride.								
1.56	0.21	0.71°	0.39°	0.32°	74.40	0.38	0.80	0.24
3.10	0.42	1.40	0.78	0.62	74.70	0.68	0.90	0.44
5.60	0.75	2.53	1.39	1.14	75.10	0.98	1.16	0.74

\* These figures were calculated from the two sets of determinations at different temperatures.

intrinsic pressure, and Walden \* has calculated the value of the ratio from determinations made at the boiling-point. If surface tension is really proportional to intrinsic pressure, the same ratio should hold at ordinary temperatures, nor is there anything in Walden's calculations inconsistent with this. Accordingly we may write

$$\delta\Pi = 75.3 \delta\sigma,$$

$\delta\Pi$  being the increment of intrinsic pressure due to the non-aggregated solute particles and  $\delta\sigma$  the corresponding increment of surface tension in dynes per centimetre. Since 1000 atmospheres increase of pressure depress the freezing-point of water  $8^{\circ}.5$ , the depression,  $\delta D$ , corresponding to the increase of internal pressure  $\delta\Pi$  would be

$$\begin{aligned}\delta D &= \frac{\delta\sigma \times 75.3 \times 8^{\circ}.5}{1000} \\ &= 0.64 \delta\sigma^{\circ}. \quad . . . . . (v)\end{aligned}$$

The correspondence between the observed increases in the depression and the calculated values of  $0.64 \delta\sigma$ , shown in the last column of the table is remarkable. It appears, therefore, that the observed increases in the depression of the freezing-point of aqueous solutions of salts above that due to a normal solute, are caused by the enhanced intrinsic pressures resulting from the greater molecular fields of the solutes. For non-aggregated salts the increased depression is given by the equation (v.). Incidentally this may be regarded as an experimental verification of Walden's relation.

The Science Museum,  
South Kensington,  
London, S.W. 7.

LXXVI. *On the Failure of the Reciprocity Law  
in Photography.* By R. A. MALLET, B.A.†

THE failure of the photographic plate with a silver bromide-gelatine emulsion to obey the "Reciprocity Law" of Bunsen and Roscoe was first observed by Abney ‡. The first quantitative work on the subject was done by Schwarzschild §, who proposed as an empirical "Law of

\* *Zeit. physik. Chem.* vol. lxvi. p. 385 (1909).

† Communicated by Prof. T. R. Merton, F.R.S.

‡ *Proc. Roy. Soc.* liv. p. 143 (1893).

§ *Astrophysical Journ.* xi. p. 89 (1900).

Blackening" the following relation :

$$S = kIT^p,$$

where  $S$  is the degree of blackening,  $I$  the intensity of the incident light,  $T$  the time of exposure, and  $k$  and  $p$  are constants. The constant  $k$  is fully discussed by Plotnikow \*, and depends on several factors, mainly on the thickness and composition of the film. The exponent  $p$  is known as the Schwarzschild constant. Its value was determined by Schwarzschild for Schleussner plates, which he exposed to the light of a normal benzene lamp at various distances for varying lengths of time, measuring the depth of blackening by comparison with a scale of blackness standards made by means of a Scheiner sensitometer. He found  $p = 0.86$ .

Other workers in this field are Becker and Werner †, Leimbach ‡, Helmick § who used a Lemon spectrophotometer, Stark || who used a König-Martin spectrophotometer, and Plotnikow who used a Kruss polarization colorimeter. Apart from the fact that all these workers have obtained their results by methods depending on the comparison of light and shade by eye, and that their numerical results vary somewhat, no one appears as yet to have suggested any physical meaning for the constant  $p$ . It is, in fact, uncertain whether it depends on the density, and whether it is constant for a given make of plate under all conditions. Stark has shown that it is subject to considerable variation over abnormal ranges of exposure, and he and others have shown that it varies somewhat with the wave-length of the light used. Schwarzschild (*loc. cit.*) used both light and heavy blackening, and found it to remain constant, but some further investigation seemed desirable.

It was decided to use a method which did not depend on visual comparison of varying shades of blackness, and to this end a Goldberg wedge screen was introduced between the plate and the source of light. This was carried out as follows :—

A brass plate, having in it a slit about three inches high and three millimetres wide, was let into a wooden board, having at the back a recess of such size that a quarter-plate wedge screen fitted in closely, in such a position that the slit was opposite the middle of the wedge. Immediately behind the wedge was placed the plate-holder, consisting of

\* *Lehrbuch d. Photochem.* p. 667.

† *Zeit. f. wiss. Phot.* x. p. 382 (1907).

‡ *Zeit. f. wiss. Phot.* x. p. 137 (1909).

§ *Phys. Rev.* xvii. 2, p. 142 (1921).

|| *Ann. d. Phys.* xxxv. 3, p. 461 (1911).

an ordinary single metal dark slide, so arranged that it could be slid across the slit and stopped in any of several positions by means of a small spring loaded plunger. The wooden board was fixed to the bench in an upright position, and a well-fitting wooden shutter arranged to slide across the front of the slit. This shutter was worked by hand. The source of light was a 36-watt 12-volt gas-filled motor headlamp bulb, connected in parallel with a voltmeter to a 12-volt accumulator battery. This battery was connected through a suitable resistance to the town mains so as to form a charging circuit. In the course of three months the voltmeter reading fell by 0.2 volt, so that the drop during one experiment was negligible. The lamp was enclosed in a light-tight box with a square hole cut in the front, with the object of removing irregularities due to stray reflexion from the walls of the room. The light was used at a constant distance of about one metre from the plate, at which distance even illumination over the whole of the slit was obtained. All exposures were timed by a stop-watch, the error in moving the shutter being of the order of 1/10th of a second, which may be neglected, in view of the length of the exposures used.

It is evident that with an arrangement of this kind, if a plate be exposed behind the wedge, a line will be photographed on it, the length of which will be a function of the time of exposure and of the intensity of the incident light. Furthermore, if two lines are photographed side by side and the time of exposure varied while the intensity is kept constant, then

$$I_0 e^{-\rho t_0} T_0^p = I_1 e^{-\rho t_1} T_1^p,$$

$$\text{and hence} \quad p = \frac{\rho(t_0 - t_1)}{\log T_0 - \log T_1},$$

where  $\rho$  is the wedge constant,  $T_0$  and  $T_1$  the times of exposure,  $t_0$  and  $t_1$  the lengths of the lines.

#### *Determination of the Wedge Constant.*

The wedge constant was determined for the light used by exposing Paget "Half-Tone" plates behind it to light of two different intensities, the time of exposure being kept constant. The intensities were in the ratio 1 : 25, the variation being obtained by altering the distance between the light and the plate from one metre to five. Then, since  $T_0 = T_1$ ,

$$I_0 e^{-\rho t_0} = I_1 e^{-\rho t_1},$$

$$\text{and hence} \quad \rho = \frac{\log I_0 - \log I_1}{t_0 - t_1}.$$

The following are the values obtained :—

Exposure (mins.).	$t_0$ (mm.).	$t_1$ (mm.).	$\rho$ .
3.0	33.10	14.79	0.0754
	32.96	14.65	0.0764
3.0	34.92	16.34	0.0740
2.5	34.87	15.80	0.0733
	34.72	15.51	0.0728
2.5	36.72	18.64	0.0773
	35.66	16.48	0.0729
2.5	34.08	16.23	0.0783
	33.98	15.24	0.0746
2.5	35.54	17.74	0.0725
2.5	46.07	27.34	0.0746

In the case of the last of the above results the plate used was a Wratten "Instantaneous," which is considerably faster than the Paget. The mean of the above is 0.0747, with a probable error of  $\pm 0.0004$ .

The mean obtained is somewhat higher than the value given by the manufacturers, Messrs. Ilford, in their calibration of the wedge used, but this is accounted for by the fact that the wedge constant increases in the violet and ultra-violet. Toy & Ghosh\*, who investigated this point, found that the value of  $\rho$  begins to rise at a wave-length of about 4500 Å, at which point the density of their wedge was 1.25. The density at 4000 Å they found to be 1.6 and at 3000 Å about 3.5. A usual method of calibration is to focus the (small) filament of an electric lamp on various parts of the wedge, and to throw the spot of light passing through on to a white screen. Light from a similar source is passed through two Nicol prisms on to an adjacent portion of the same screen, and the two spots adjusted by means of the nicols to the same intensity. Since the normal photographic range extends further into the ultra-violet than the visual range, the value for  $\rho$  given by this method will be lower than that obtained by the photographic method.

#### *Determination of the Schwarzschild Constant.*

Three types of plate were used, so chosen as to give a large variation of properties. They were the Paget "Half-Tone," the Wratten "Instantaneous," and the Imperial "Eclipse." The Paget "Half-Tone" is a process plate, about one-third faster than wet collodion plates, and giving great contrast. The Imperial "Eclipse" is one of the fastest plates obtainable, and the Wratten "Instantaneous" is intermediate between the two, being a medium slow landscape plate.

\* Phil. Mag. Dec. 1920, p. 775.



The approximate relative speeds of these plates were obtained by exposing a specimen of each behind the wedge to light of the same intensity for the same length of time, and measuring the lengths of the lines obtained as nearly as possible without further treatment of the plates after development. Then, at the end of each line,

$$I(ST)^p e^{-\rho t} = e^k,$$

where  $S$  is the speed of the plate and  $e^k$  is a constant.

Since  $p$  is not identical for each plate, it is necessary to reduce all lines to a standard length, and take the ratio of the actual time to the time for that length as proportional to the speed. If  $t_1, t_2$ , etc. are the actual lengths of the lines, and  $t_0$  the standard length, then

$$t = \frac{\log I_0 - k + p \log (ST)}{\rho}$$

$$\text{and } t_0 = \frac{\log I_0 - k + p \log (ST_0)}{\rho};$$

$$\therefore \log \frac{T}{T_0} = \frac{\rho}{p} (t - t_0) = \log kS,$$

$$\therefore \log \frac{S_1}{S_2} = \frac{\rho}{p_1} (t_1 - t_2) + \left( \frac{\rho}{p_1} - \frac{\rho}{p_2} \right) (t_2 - t_0).$$

For Paget plates .....  $\rho/p = 0.0864, t = 21.3$

„ Wratten plates .....  $\rho/p = 0.0884, t = 38.0$

„ Imperial plates .....  $\rho/p = 0.0884, t = 46.7$ .

$t_0$  was taken as 35, which is approximately the mean value of  $t$ . From these figures the relative speeds of the plates are roughly :—Paget 1, Wratten 29, Imperial 165.

The Schwarzschild constant was determined by photographing lines on the plate with long and short exposures alternately, the intensity of the light being kept constant throughout, and the duration of the long exposures being usually one hundred times that of the short. The actual times of exposure are given in the table below. In the case of the Wratten and Imperial plates, the intensity of the incident light was reduced to a convenient extent by interposing one or two neutral screens between the source of light and the wedge, the screen being let into the front of the box in which the light was enclosed at a distance of about 5 cm. from the filament. This was necessary, as, owing to the sensitivity of these plates, the exposures would otherwise have had to be made too short to admit

of accuracy in the timing. The plates were fully developed in hydroquinone and caustic soda developer, and "cut" by a few seconds' immersion in potassium ferricyanide to remove the slight chemical fog and to give a more easily measurable end to the line. After this treatment, the Paget, and in one or two instances the Wratten, plates could be measured directly, but in other cases the plates had to be printed onto Paget's, and one, or sometimes two, further transparencies made before it was possible to measure them. The plates from which the wedge constant was determined were treated in the same manner. All measurements were made on a Hilger travelling microscope, and are accurate to  $\cdot 1$  mm., and in some cases to  $\cdot 01$  mm.

As is well known, irregularities occur near the edges of a plate. For this reason, only two long and two short lines were made on each plate, and thus only the central portions were used.

It will be seen that the results for the same type of plate differ appreciably, but this is to be accounted for by variations in the thickness of the film on the plate, and the errors arising in this manner are eliminated by taking the mean of a considerable number of determinations on different plates.

Paget Plates.		Wratten Plates.		Imperial Plates.	
Exposure (seconds).	<i>p.</i>	Exposure.	<i>p.</i>	Exposure.	<i>p.</i>
32 & 15976	0.830	10 & 1020	0.874	20 & 2000	0.843
		10 & 1000	0.840		0.843
32 & 15976	0.833	10 & 1000	0.867	10 & 1000	0.868
	0.900	10 & 1020	0.861		0.880
60 & 6000	0.867	10 & 1000	0.857	10 & 1000	0.861
	0.879		0.798		0.897
60 & 6000	0.856	10 & 1000	0.867	10 & 1000	0.854
	0.873		0.834		0.861
45 & 4500	0.792	10 & 1000	0.831	10 & 1000	0.765
	0.817		0.840		0.830
45 & 4560	0.962	5 & 550	0.878	10 & 1000	0.847
	0.902				0.837
45 & 4500	0.861	10 & 1000	0.834	10 & 1000	0.803
	0.871		0.815		0.865
	0.865				
45 & 4500	0.847			10 & 1000	0.829
					0.846
30 & 2000	0.869				
30 & 2000	0.885				
	0.868				

From the foregoing are obtained the following mean values of  $p$  :—

Paget "Half-Tone" plates .....  $0.865 \pm 0.005$

Wratten "Instantaneous" plates .  $0.846 \pm 0.005$

Imperial "Eclipse" plates .....  $0.846 \pm 0.005$

The probable error, which is certainly not due to errors in measurement of the lengths of the lines, was calculated in the usual manner.

It is noteworthy that the mean values for the fairly slow Wratten plates and for the very fast Imperial plates agree exactly. Becker and Werner (*loc. cit.*) have stated that the value of  $p$  tends to increase with sensitivity, but this does not appear to be confirmed by the present investigation.

The question then arose as to whether  $p$  was really a constant for any one type of plate for any variations of intensity and duration of exposure within the normal range (great over-exposure, *i. e.* solarization, being left out of the question), or whether it was dependent on the intensity or on the time of exposure, or on both. Evidently, if  $p$  is constant for all conditions of time and intensity, the gradation of two lines on the plate of about equal length, but made under differing conditions, will be the same.

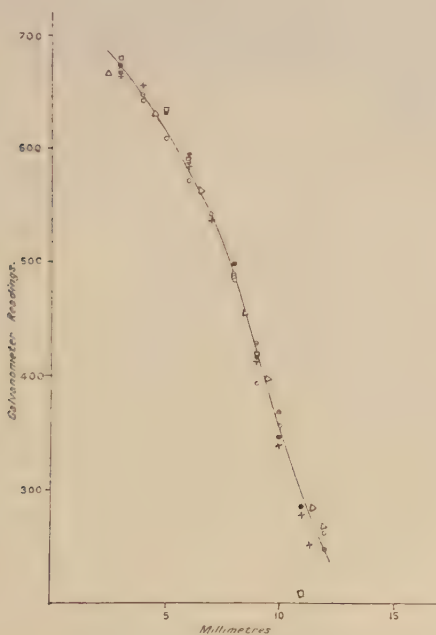
To ascertain this, two plates were prepared, having on them lines of approximately the same length, but in which the intensity and the duration of exposure were so altered that  $IT^p = \text{const.}$  Six lines were made on the two plates. The intensity of the incident light was as 1 in the case of three lines to 6.25 in the other three, and the time of exposure adjusted so that  $IT^p = 8$  in two cases and  $= 12$  in the other four.

The plates used were Paget "Half-Tone." They were fully developed but not "cut," and the relative blackening at different points of the lines was compared by means of a photometer, involving the use of a photoelectric cell and a string galvanometer which had been designed by Mr. G. M. B. Dobson, to whom I am greatly indebted for the loan of this instrument and for his assistance and advice. Owing to the limited range of the galvanometer it was possible to measure the densities of the lines only over a range of 10 to 14 mm.

The distances from the ends of the lines were plotted against the actual galvanometer readings, which have been used as an arbitrary scale of blackness. It will be seen from the figure that the gradations of the lines are identical,

despite the alterations of intensity and duration of exposure. The points represented by  $+$   $\triangle$  etc. refer to the different plates measured, and the values plotted are over the same range of density so as to show the similarity in the shape of the curves. From this it is evident that the Schwarzschild constant has a definite value for each type of plate, and that this value remains constant over a range of density extending from zero to approximately unity, since the density of the wedge used is about 0.075 per mm. and the portion of the lines considered in the curves given is about 14 mm. long.

Fig. 1.



It is further evident from a consideration of these curves that the value of the Schwarzschild constant is the same at the "threshold," *i. e.* at the point where the plate is just darkened, as at greater densities. Owing to the "cutting" of the plates used in determining the constant, the value given by them was not that at the "threshold," but the measurements made with the photoelectric cell extend to the extreme ends of the lines, and the curves coincide perfectly at this point also.

It is evident that the Schwarzschild constant has a very definite physical significance, but what this may be it is not possible to say. From the values obtained with the three types of plate it is evident that it is not greatly dependent on either the size of the grain or on whatever factors ultimately determine the sensitivity of a plate to light, but a fuller knowledge of the composition of the silver halide-gelatine emulsion and of its physical properties would seem to be necessary before a complete explanation can be arrived at.

This investigation was undertaken at the suggestion of Prof. T. R. Merton, F.R.S., to whom I am deeply indebted both for the loan of almost all the apparatus used, and for much valuable help in the course of the investigation. Thanks are also due to Mr. C. H. Bosanquet for several valuable suggestions.

Balliol College Laboratory,  
Oxford.

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LXXVII. *Magnetic Rotatory Dispersion of certain Paramagnetic Solutions.* By R. W. ROBERTS, *M.Sc.*, J. H. SMITH, *M.Sc.*, and S. S. RICHARDSON, *D.Sc.*, *A.R.C.Sc.*\*

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ONE of the anomalies met with in the examination of the Faraday effect is that, whereas the salts of iron in solution give rise to a negative rotation, those of the strongly magnetic elements, nickel and cobalt, produce a rotation of the plane of polarization in the opposite sense—that is, in the direction of the rotation produced by the great majority of compounds both inorganic and organic. In the case of cobalt sulphate the rotation, though positive, is almost zero. It is noteworthy, however, that the measurements on which such statements are based have been made only with reference to the D line or at most a few lines in the visible spectrum, and some years ago it occurred to one of us that further information might be obtained by examining the course of the rotatory dispersion in the ultraviolet. Experiments were carried out in 1916 on  $\text{CoSO}_4$ , and the spectrum photographs showed that the rotation of this salt becomes strongly negative in the ultraviolet. The principal absorption-band lies on the borders of the visible and ultraviolet, and the rotation, which has a small positive value up to the edge of the band in the visible spectrum, becomes negative where the spectrum reappears, and remains negative throughout the ultraviolet up to the point where general absorption

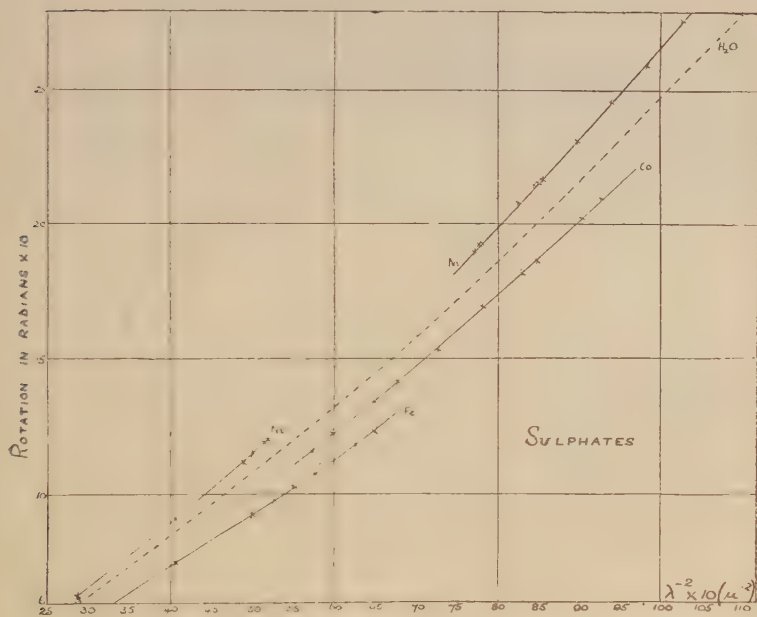
\* Communicated by Prof. L. R. Wilberforce, M.A.



cuts off the spectrum completely, which occurs in the region of 3000 Å.U.

The result with cobalt indicated that a systematic examination of the the rotation produced by paramagnetic substances in the ultraviolet would be of interest, and the present communication refers to the results obtained with the sulphates (fig. 1), chlorides (fig. 2), and acetates (fig. 3) of nickel and cobalt, also ferrous sulphate, in aqueous solution\*.

Fig. 1.



The method employed has already been described in connexion with the rotation in certain organic compounds†. The solution was contained in a short tube (1.135 cm. long) placed between the poles of the electromagnet. The rotation obtained for water showed that a reversal of the current (7 amperes) produced a change of magnetic potential 30380 cm.-gauss.

In the accompanying graphs dispersion curves are given

\* The results for nickel and cobalt sulphates were confirmed in this Laboratory in 1918 by the Rev. W. D. Ross, M.Sc.

† S. S. Richardson, Phil. Mag. vol. xxxi. p. 232.

Fig. 2.

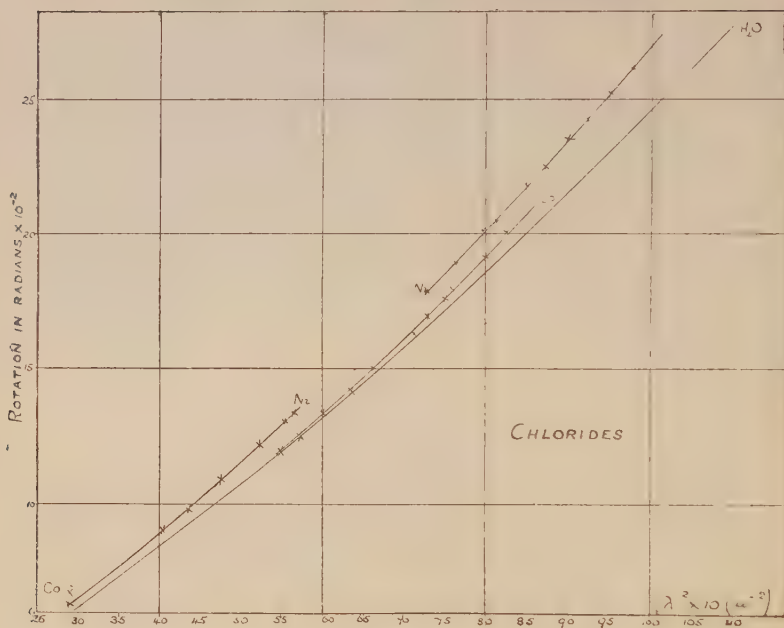
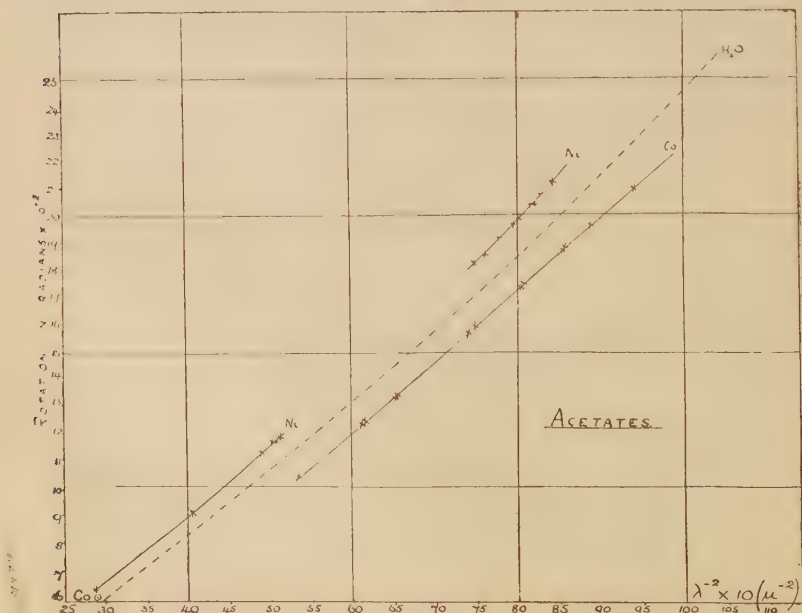


Fig. 3.



for the solutions and for pure water\*. When the water of crystallization of the salt is taken into account, the mass of water per c.c. is practically the same in the solution as it is in the case of water alone: the difference in the ordinates therefore represents the rotation produced by the salt alone.

As small differences of rotation were to be measured it was necessary to work with fairly concentrated solutions, and the graphs refer to the following concentrations:—

Nickel Chloride .....	·216 molar.
Cobalt     " .....	·625     "
Nickel Sulphate .....	·624     "
Cobalt     " .....	·594     "
Ferrous    " .....	·312     "
Nickel Acetate .....	·664     "
Cobalt     " .....	·625     "

The results indicate that the cobalt atom, like the iron atom, is capable of producing a negative rotation, but of smaller numerical value. The disappearance of this on the low-frequency side of the band may be attributable to the preponderating positive effect of the ( $\text{SO}_4$ ), ( $\text{C}_2\text{H}_3\text{O}_2$ ), or Cl ions. This view is supported by the fact that when a highly dispersive element (*e. g.*, chlorine) is present the residual negative effect in the ultraviolet is smaller, but the point requires further investigation. In the case of nickel the rotation remains positive throughout the range measured, but does not undergo the large increase in the ultraviolet which is observed with diamagnetic substances. It is possible therefore that the nickel atom, whilst not able to overbalance the positive effect of the other atoms in the salt, still exerts sufficient depression nearly to neutralize the dispersion. From this point of view, our results indicate that in respect of paramagnetism the cobalt atom occupies a position intermediate between those of iron and nickel.

The experiments are to be continued, and we hope to publish results for other paramagnetics shortly.

We beg to tender our thanks to Prof. Willerforce for the facilities and apparatus placed at our disposal and to Dr. Smeath Thomas who kindly prepared the ferrous sulphate solution.

The George Holt Physics Laboratory,  
University of Liverpool.

\* To obtain the rotation of the salts in radians per cm.-gauss the graph-readings must be multiplied by  $6.616 \times 10^{-5}$ .

LXXVIII. *Colour-Vision Theories in Relation to Colour-Blindness.* By F. W. EDRIIDGE-GREEN, C.B.E., M.D., F.R.C.S., *Special Examiner and Adviser to the Board of Trade on Colour Vision and Eyesight* \*.

THE importance of colour-blindness as a key to any colour-vision theory does not seem to be sufficiently recognized, though the fact was well known to Helmholtz †, who showed that Hering's theory explained the facts of colour mixing quite as well as his own, and stated: "As far as I see, there is no other means of deciding on the elementary colour sensations than the examination of the colour-blind." This cannot be too widely known, because any other method assumes that the three-sensation theory is correct, and is useless when this theory is denied. As has been shown by Houstoun ‡, my non-elemental theory explains the facts of colour mixing quite as well as either of the above mentioned. Recently I have examined about 200 cases of colour-blindness by colour-mixing methods as well as my own, in order to ascertain certain facts of crucial importance in deciding between an elemental and a non-elemental theory.

*Relation of Luminosity to Colour.*

If the sensation of white were compounded of the addition of three elementary processes and one of these processes were subtracted, the position of the apex of the luminosity curve would not be the same in the colour-blind as in the normal. It is, however, well known that there are numerous dichromics who have a luminosity curve similar to the normal.

A case of colour-blindness regarded from the point of view of a three-sensation theory may, for instance, be one-half red-blind; the composition of the theoretical white will then be  $\frac{1}{2}R + 1G + 1V$ . As far as luminosity is concerned, this white may be compared with light of various wave-lengths by the colour-blind subject, just as normal white is by the normal sighted. Now, as the apex of the luminosity curve depends upon the point where the aggregate stimulation of the three theoretical sensations is greatest in terms of luminosity, this apex will be displaced towards the point of maximum stimulation of the other sensation, namely green, the luminosity of the blue being so low as to be negligible. Numerous cases can, however, be found in which the apex of

\* Communicated by the Author.

† *Physiologische Optik*, 2nd edition, p. 377.

‡ *Phil. Mag.* vol. xxxviii. p. 402 (1919).

the luminosity curve is at the same point as the normal. A striking case of this kind was examined recently—a dichromic with shortening of the red end of the spectrum; the apex of his luminosity curve for the light of the Pointolite arc was at  $\lambda 585\mu\mu$ , which is the apex for the normal-sighted.

*Explanation of the facts of Colour-Blindness.*

The facts of colour-blindness are quite inconsistent with any three-sensation theory. Supporters of such an elemental theory have in many cases contented themselves with describing a case of colour-blindness in the terms of the theory without showing that the ascertained facts are consistent with the theory. No one, for instance, has shown how on an elemental theory 50 per cent. of dangerously colour-blind can get through the now obsolete wool test. On the non-elemental theory the explanation is easy enough: the man has defective colour discrimination, but not sufficient to prevent him matching wools in favourable circumstances, particularly when colour names are not used. On an elemental theory, why should the trichromic mark out about half the number of monochromatic divisions in the spectrum, designate yellow as red-green, and have an increased simultaneous colour contrast? When there are three definite colour sensations, how can colour-blindness be explained? The recent paper by Houstoun\* should be read on this point.

*The Anomalous White Equation without Colour-Blindness.*

Just as a man may make an anomalous Rayleigh equation without any evidence of colour-blindness, so may a man make an anomalous white equation without being colour-blind†. As an example of this, a man was examined who presented no sign of colour weakness. He passed my card test, lantern test, and spectrometer with the ease and accuracy of an absolutely normal-sighted person. His luminosity curve was taken by the flicker method, and corresponded with the normal. The wave-length of the apex of the luminosity curve was at  $585\mu\mu$ , which is the normal point. When, however, his white equation was taken, he put only 8 scale divisions of green, instead of  $13\frac{1}{2}$  or 14, which is normal, and the mixed light appeared red to the normal-sighted. An important fact was noted—namely, that after fatigue with red of the region of  $\lambda 670\mu\mu$ , the

\* Proc. Roy. Soc. Edin. vol. xlii. pt. i. no. 7, p. 75 (1922).

† Proc. Roy. Soc., B. vol. lxxxvi. p. 164 (1913).



equation changed for him in the same way as for the normal-sighted\*. After fatigue with the red light, he required only 4 scale divisions instead of 8. It is quite obvious that this was not a case of partial red-blindness from the point of view of the three-sensation theory, though he was not as sensitive to the red end of the spectrum as the normal sighted.

### *The White Equation and Colour-Blindness.*

The colour-blind have been classified by some as red or green-blind, in accordance with their white equations—that is, the amount of pure spectral red, green, and violet required to match a simple white; those who put too much red in the equation being classed as red-blind, and those who put too much green in the equation being classed as green-blind. There are, however, many who, whilst agreeing with the normal equation, are quite satisfied when a considerable additional amount of green or red is added to the equation. This explains why in certain cases some have been described as red-blind by one observer and green-blind by another.

A remarkable fact, which does not seem to have been previously observed, is that many colour-blind persons who strongly object to the normal match, but are satisfied with an anomalous equation, will completely agree with the normal equation when the comparison white light is increased in intensity so that it is much too bright to a normal-sighted person. This clearly shows that the normal mixed white produces the same effect as far as colour is concerned, but has a more powerful effect as to luminosity. This is in complete accordance with other observations, and is found in those cases in which there is abrupt and slight shortening of the red end of the spectrum. If there be shortening of the red end of the spectrum which does not affect  $\lambda 670\mu\mu$ , and  $\lambda 670\mu\mu$  has its normal light value, the mixed light will be more luminous than the simple white in proportion to the shortening. This portion of red light not producing any effect has to be subtracted from the white light. These facts are quite inconsistent with a hypothetical red sensation which is affected by light of all wave-lengths. Another illustration may make this point clear. A man with shortening of the red end of the spectrum and normal colour discrimination will put together as exactly alike a pink and a blue or violet much darker. If, however, the pink and blue be viewed by a normal-sighted person through a blue-green glass which cuts off the red end of the spectrum,

\* Proc. Roy. Soc., B. vol. xcii. p. 232 (1921).

both will appear identical in hue and colour. This proves conclusively that the defect is not due to a diminution of a hypothetical red sensation, because all the rays coming through the blue-green glass are supposed to affect the red sensation, and yet we have been able to correct the erroneous match by the subtraction of red light. On the other hand, there are colour-blind persons who, whilst disagreeing with the normal white equation, agree with it when the comparison white is diminished in intensity.

A totally erroneous view of a case may be obtained through methods based on the three-sensation theory. A man may be examined and found to put too much green in his white equation; he is therefore classified as partially green-blind. Further examination shows that he can pass the wool test, but fails to see a deep red light formed by rays from the red end of the spectrum. The fact that he is insensible to these rays explains the facts of his case, including his error in colour mixing. As certain red rays are invisible to him, these have to be subtracted from white light. If his white could be seen by a normal-sighted person, it would appear greenish white. Therefore, if the colours used in the white equation have their normal value, he will put more green than normal in the equation, as he is really matching a greenish white.

Even the facts of colour mixing are far more satisfactorily explained by a non-elemental than by an elemental theory. For instance, a considerable amount of one spectral colour may be added to another without altering its appearance.

Houstoun has shown very clearly that from a mathematical and physical point of view only one substance is necessary, and that there is no evidence of more than one. All the facts tend to show that the visual purple is the visual substance, that the cones are the terminal perceptive visual organs, and that the rods are not perceptive elements, but are concerned with the formation and distribution of the visual purple. Vision takes place by stimulation of the cones through the photo-chemical decomposition of the liquid surrounding them, which is sensitized by the visual purple \*. The ends of the cones being stimulated through the photo-chemical decomposition of the visual purple by light, a visual impulse is set up which is conveyed through the optic-nerve fibres to the brain. The character of the stimulus and impulse differs according to the wave-length of the light causing it. In the impulse itself we have the

\* 'The Physiology of Vision,' G. Bell & Sons, London, 1920, p. 134.

physiological basis of the sensation of light, and in the quality of the impulse the physiological basis of the sensation of colour. But though the impulses vary according to the wave-length of the light causing them, the retino-cerebral apparatus is not able to distinguish between the character of adjacent stimuli, not being sufficiently developed for the purpose. At most seven distinct colours are seen, whilst others see, in proportion to the development of their colour-perceiving centres, six, five, four, three, two, or none. This causes colour-blindness, the person seeing only two or three colours instead of the normal six, putting colours together as alike which are seen by the normal-sighted to be different. In the degree of colour-blindness just preceding total, only the colours at the extremes of the spectrum are recognized as different, the remainder of the spectrum appearing grey.

## LXXIX. *Natural Convective Cooling in Fluids.*

By A. H. DAVIS, M.Sc.\*

[From the National Physical Laboratory.]

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Cooling Power of Fluids.

### *Introduction.*

BY general reasoning from the principle of similitude†, introducing certain plausible assumptions, it is possible to obtain the following formula to represent the heat loss by natural convection from similar bodies similarly immersed in viscous fluids.

$$hL/k\theta = F(c^2 g L^3 a \theta / k^2) f(c\nu/k), \quad . \quad . \quad . \quad (1)$$

\* Communicated by the Author.

† Davis, Phil. Mag. xl. p. 692 (1920).

where

$h$  = heat loss per unit time per unit area of the body,

$k$  = thermal conductivity of the fluid,

$c$  = capacity for heat of the fluid per unit volume,

$\nu$  = kinematical viscosity of the fluid,

$\theta$  = temperature excess of the body,

$\alpha$  = coefficient of density reduction of the fluid per degree rise of temperature,

$g$  = acceleration due to gravity,

$L$  = linear dimensions of the body.

For gases,  $\alpha/k$  is practically constant, and so experiments with them cannot reveal the effects of this term. However, the formula, restricted by its omission, has already been shown for gases to be in good general agreement with experimental results. In the investigation, early work on miscellaneous small bodies has been considered\*, and also data for moderately heated large vertical surfaces from 2 inches to 9 feet in height†. Particular attention has been given to the case of wires and long cylinders‡, owing to the wide range of size, temperature excess, gas nature and pressure for which results were available.

Liquids, however, cover a wide range of values of  $c\nu/k$ , and so experiments on the cooling of wires in liquids were undertaken to study the effects of this term.

But, further, it was suspected that  $g$  and  $\nu$  might always occur together in the equation in the form  $g/\nu$ , for any steady velocity of the viscous streams will be determined by a balance between the accelerating forces due to gravity and the retardation due to viscosity. The formula would then take the simple form

$$hL/k\theta = F(L^3\theta g \alpha c/k\nu). \quad . \quad . \quad . \quad . \quad (2)$$

The present paper investigates the possibility of such a simplification, and therefore consists of two main parts—one theoretical, in which more formal consideration is given to convection in a viscous fluid; and the other experimental, where convective cooling of wires is studied for a series of fluids of different viscosity with a view to experimental verification of the formulæ put forward.

\* Davis, *loc. cit.*

† Dept. of Scientific and Industrial Research. Food Investigation Board Special Report, No. 9.

‡ Davis, *Phil. Mag.* xliii. p. 329 (1922).

## Part I.—THEORETICAL.

Convective cooling is taken to refer to the total heat transfer from a hot body by the medium of a fluid moving past the surface. Such cooling is said to be "natural" or "free" when the fluid is still, except for the streams set up by the heat from the hot body itself, and is said to be "forced" when the body is immersed in a fluid stream, usually considered to be moving with such velocity that the currents set up by the hot body itself are negligible. The present paper is limited to natural convection.

In 1820, Fourier\* stated the equation of heat conduction in a moving fluid, and in 1881, Lorenz†, upon certain assumptions, gave a formula for heat loss by natural convection for the special case of a vertical plane surface immersed in an infinite viscous fluid. In 1901, Boussinesq‡, dealing with inviscid fluids, gave a general solution of the problem of natural convection from heated solids in infinite fluid media.

The following investigation follows Boussinesq closely, but introduces the modifications necessary in extending the inquiry to viscous fluids.

Adopting the same mathematical symbols as those already used, let us consider the natural convective cooling of a hot body immersed in an infinite viscous medium and maintained at a certain temperature,  $\theta$  degrees in excess of that of the liquid at infinite distance, to which all temperatures are referred.

Let  $\rho$  and  $\nu$  be respectively the density of the fluid and its kinematical viscosity. For an element of the fluid at the point  $x, y, z$ , let  $\tau, u, v, w, P$  be the temperature excess (assumed steady, *i. e.* independent of time  $t$ ), the three components of its velocity, and the non-hydrostatic part of its pressure. For elements of the fluid at infinite distance these quantities are all zero.

Let us assume that the dilatation of the fluid by heat is negligible except in so far as the weight of unit volume is altered, so that it occurs in the equations only when multiplied by  $g$ . Let  $\rho\alpha$  be the reduction in weight produced in unit volume by unit rise of temperature.  $\rho\alpha\tau$  thus being the total reduction effected. The axis of  $z$  being vertical, the hydrodynamical equations of continuity and of motion are

$$\left. \begin{aligned} \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} &= 0, & \frac{1}{\rho} \frac{\partial P}{\partial x} &= -u' + \nu \nabla^2 u, \\ \frac{1}{\rho} \frac{\partial P}{\partial y} &= -v' + \nu \nabla^2 v, & \frac{1}{\rho} \frac{\partial P}{\partial z} &= -g\alpha\tau - w' + \nu \nabla^2 w, \end{aligned} \right\} (3)$$

\* Fourier, *Mémoires de l'Académie*, xii. p. 507 (1820).

† Lorenz, *Ann. der Physik*, xiii. p. 582 (1881).

‡ Boussinesq, *Comptes Rendus*, cxxxii. p. 1382 (1901).



$u'$ ,  $v'$ , and  $w'$  being the accelerations of the fluid parallel to the axes.

If  $k$  be the thermal conductivity of the fluid and  $c$  its heat capacity per unit volume, then  $\tau'$ , the rate of change of temperature for a given particle with respect to time, is given by

$$\tau' = \frac{k}{c} \nabla^2 \tau. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Also, the derivative  $\tau'$ , like the derivatives  $u'$ ,  $v'$ ,  $w'$  of the velocities, is obtained by finding the increase in  $\tau$  when  $x$ ,  $y$ ,  $z$ , increase by  $u dt$ ,  $v dt$ , and  $w dt$ ; in this way we have the quadruple equation

$$(u', v', w', \tau') = u \frac{\partial(u, v, w, \tau)}{\partial x} + v \frac{\partial(u, v, w, \tau)}{\partial y} + w \frac{\partial(u, v, w, \tau)}{\partial z}. \quad . \quad . \quad . \quad (5)$$

To the five differential equations (3) and (4) it is necessary to add the following seven boundary conditions, in the first of which,  $l$ ,  $m$ ,  $n$ , denote the three direction-cosines of the normal drawn from the interior of the fluid to any element of surface of the body.

$$\left. \begin{array}{l} \text{At the surface of the solid } u=v=w=0 \text{ and } \tau=\theta, \\ \text{At infinite distance } (P, u, v, w, \tau)=0. \end{array} \right\} \quad (6)$$

In words, at the surface of the solid the fluid takes the temperature  $\theta$  of the solid, and the velocity is zero.

Following Boussinesq, let us endeavour to replace the independent variables  $x, y, z$  and the functions  $\tau, u, v, w, P$  by others,  $\xi, \eta, \zeta, T, U, V, W, \Pi$ , respectively proportional to each of them, but whose ratios are chosen in a manner to eliminate the parameters  $\theta, ga, k/c, \rho, \nu$ .

Let us consider the following substitutions :

$$\left. \begin{array}{l} \xi = \left( \frac{\theta g a c}{k \nu} \right)^{1/3} x, \quad \eta = \left( \frac{\theta g a c}{k \nu} \right)^{1/3} y, \quad \zeta = \left( \frac{\theta g a c}{k \nu} \right)^{1/3} z, \\ \tau = \theta T, \quad u = \left( \frac{\theta g a k^2}{c^2 \nu} \right)^{1/3} U, \quad v = \left( \frac{\theta g a k^2}{c^2 \nu} \right)^{1/3} V, \quad w = \left( \frac{\theta g a k^2}{c^2 \nu} \right)^{1/3} W, \\ P = \rho \left( \frac{\theta^2 g^2 k \nu}{c} \right) \Pi. \end{array} \right\} \quad (7)$$

It is readily found that the substitutions eliminate the parameters satisfactorily if  $c\nu/k$  is a constant and equal to unity. For liquids  $c\nu/k$  may have very large values (glycerine 8000, etc., see later), but for gases, as indicated by the Kinetic Theory, it is constant and approximately

equal to unity. For gases, therefore, the above substitutions should be fairly satisfactory on this ground.

There is an alternative condition under which the substitutions are satisfactory, even without  $cv/k$  being a constant. The condition is that the accelerations  $u', v', w'$  of the particle shall be negligible compared with  $\nu \nabla^2 u$ , etc., which would appear to be justifiable for very viscous fluids. It implies that on coming into the region of the hot body a particle of the fluid almost immediately takes up its final velocity and suffers but little subsequent acceleration.

Consequently, the above substitutions appear satisfactory, and the differential equations (3) and (4) take the following form. ( $U' V' W'$  may be retained if  $cv/k=1$ , but otherwise they must be omitted since  $u', v'$ , and  $w'$  are neglected \*).

$$\left. \begin{aligned} \frac{\partial U}{\partial \xi} + \frac{\partial V}{\partial \eta} + \frac{\partial W}{\partial \zeta} &= 0, & T' &= \frac{\partial^2 T}{\partial \xi^2} + \frac{\partial^2 T}{\partial \eta^2} + \frac{\partial^2 T}{\partial \zeta^2}, \\ \frac{\partial \Pi}{\partial \xi} &= -U' + \left( \frac{\partial^2 U}{\partial \xi^2} + \frac{\partial^2 U}{\partial \eta^2} + \frac{\partial^2 U}{\partial \zeta^2} \right), \\ & \frac{\partial \Pi}{\partial \eta} = -V' + \left( \frac{\partial^2 V}{\partial \xi^2} + \frac{\partial^2 V}{\partial \eta^2} + \frac{\partial^2 V}{\partial \zeta^2} \right), \\ & \frac{\partial \Pi}{\partial \zeta} = -T - W' + \frac{\partial^2 W}{\partial \xi^2} + \frac{\partial^2 W}{\partial \eta^2} + \frac{\partial^2 W}{\partial \zeta^2}, \end{aligned} \right\} \quad (8)$$

$$\text{where } (U', V', W', T') = U \frac{\partial(U, V, W, T)}{\partial \xi} + V \frac{\partial(U, V, W, T)}{\partial \eta} + W \frac{\partial(U, V, W, T)}{\partial \zeta}.$$

\* I am indebted to Mr. W. G. Bickley, M.Sc., for the following notes:—

(a) If  $cv/k$  is not equal to unity, equations 8 are mathematically correct if we write  $\frac{k}{cv} U'$  for  $U'$ , etc. Evidently, if  $cv/k$  is large, the term  $\frac{k}{cv} U'$  is correspondingly small and may be omitted. Retaining it, however, the solution of (8) becomes

$$\tau \quad u, v, w \quad P \\ 0, \quad \left( \frac{\theta g a k^2}{c^2 \nu} \right)^{1/3}, \quad \rho \left( \frac{\theta^2 g^2 a^2 k \nu}{c} \right)^{1/3} = \text{definite functions of} \quad \left\{ \left( \frac{\theta g a c}{k \nu} \right)^{1/3} (x, y, z); \frac{cv}{k} \right\}.$$

The experimental curve shows that the occurrence of  $cv/k$  in these functions is in such a manner that large variations in  $cv/k$  have imperceptible effects.

(b) Equation (5), and the resulting one (8), would be more general if the term  $\frac{\partial(u, v, w, \tau)}{\partial t}$  were introduced on the left-hand side. This would include unsteady motion, but would in no way affect the changes of variables.

Also, let us put the equation of the solid in the form

$$f\left[\left(\frac{\theta gac}{kv}\right)^{1/3} x, \left(\frac{\theta gac}{kv}\right)^{1/3} y, \left(\frac{\theta gac}{kv}\right)^{1/3} z\right] = 0. \quad (9)$$

Thus, if the coefficient  $(\theta gac/kv)^{1/3}$  changes, this amounts to considering, instead of the actual solid, similar bodies having linear dimensions inversely proportional to this coefficient. Then the direction-cosines  $l, m, n$ , of the normal will remain the same at corresponding points, and the boundary conditions become

$$\left. \begin{array}{l} \text{At the surface } U=V=W=0 \quad \text{and} \quad T=1, \\ \text{At the distance } \sqrt{\xi^2 + \eta^2 + \zeta^2} \text{ infinite } (\Pi, U, V, W, T)=0. \end{array} \right\} \quad (10)$$

The system of equations (8) and (10) determine  $(U, V, W, T, \Pi)$  as the functions of  $\xi, \eta, \zeta$ , and substituting in the integrals for the eight new variables their equivalents as given by (7), we have five relations of the form

$$\left\{ \begin{array}{l} \frac{\tau}{\theta}, \quad \frac{(u, v, w)}{\left(\frac{\theta gac}{c^2 v}\right)^{1/3}}, \quad \frac{P}{\rho \left(\frac{\theta^2 g^2 a^2 kv}{c}\right)^{1/3}} \end{array} \right\} = \text{definite functions of} \left\{ \begin{array}{l} \left(\frac{\theta gac}{kv}\right)^{1/3} x, \quad \left(\frac{\theta gac}{kv}\right)^{1/3} y, \quad \left(\frac{\theta gac}{kv}\right)^{1/3} z. \end{array} \right\} \quad (11)$$

The flux of heat furnished in unit time by unit area of such a body, equal to that which the contiguous liquid layer communicates to the interior of the fluid, is given by

$$k \left( l \frac{\partial \tau}{\partial x} + m \frac{\partial \tau}{\partial y} + n \frac{\partial \tau}{\partial z} \right).$$

Introducing the new variables, we have then

$$h = k(\theta gac/kv)^{1/3} \theta \left( l \frac{\partial T}{\partial \xi} + m \frac{\partial T}{\partial \eta} + n \frac{\partial T}{\partial \zeta} \right). \quad (12)$$

At corresponding points of the surfaces  $f(\xi, \eta, \zeta) = 0$  limiting the bodies considered, the direction-cosines  $l, m, n$  and the derivatives  $\frac{\partial T}{\partial(\xi, \eta, \zeta)}$  have the same values respectively; so the trinomial coefficient is a function of the shape and orientation of the bodies only.

Thus the result may be stated in the following form. For a family of similar bodies similarly oriented, and having linear dimensions  $L$  given by

$$L \propto (\theta gac/kv)^{-1/3}, \quad \text{i. e. } (L^3 \theta gac/kv) = \text{const.},$$

the heat loss per unit area from corresponding points is given by

$$h \propto k\theta(\theta gac/kv)^{1/3}, \quad \dots \dots (13)$$

and this will also be true if  $h$  represents mean heat loss for the whole model. So for bodies of this shape and orientation we have

$$h = k\theta(\theta gac/kv)^{1/3} f(L^3\theta gac/kv), \quad \dots \dots (14)$$

which may be written

$$hL/k\theta = F(L^3\theta gac/kv). \quad \dots \dots (15)$$

This equation is the simplified form of equation (1) it was desired to establish, and it has been put to the test of experiments in a later part of this paper. It is desirable to notice here one point in connexion with it.

For a series of fluids for which  $cv/k$  is constant, the equation may readily be shown to agree with that obtained by Boussinesq for inviscid fluids; *i. e.* Boussinesq's grouping of variables for inviscid fluids is satisfactory for viscid fluids for which  $cv/k$  is constant. This equivalent grouping is given by omitting  $(cv/k)$  from formula (1).

## Part II.—EXPERIMENTAL.

### *Formulae.*

For long horizontal wires of diameter ' $d$ ' it may readily be shown that formulæ (1) and (2) may be rewritten as follows in terms of the heat loss  $H$  per unit length of wire per degree temperature excess:

$$\left. \begin{aligned} H/k &= F(c^2gd^3a\theta/k^2) f(cv/k), \\ H/k &= F(d^3\theta gac/kv). \end{aligned} \right\} \dots \dots (16)$$

When  $cv/k$  is a constant, the equations are identical in form and, consequently, evidence for diatomic gases already shown elsewhere to be in agreement with one of these expressions is necessarily in agreement with the other.

If  $cv/k$  is not constant, the second equation is a special case of the first. The experiments now to be described on the cooling of wires in liquids will indicate the form of the  $cv/k$  term in (16) and also whether the simpler expression is satisfactory.

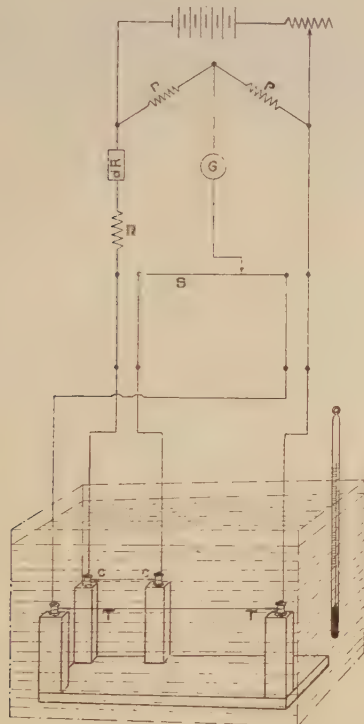
### *Apparatus.*

The method of experiment consisted in stretching a wire horizontally at a convenient depth in a vessel full of the liquid under examination, and measuring the electric energy

supply necessary to maintain a measured temperature difference between the wire and the general body of the liquid. The electric energy supplied was determined from the measured current through the wire, and from its resistance as obtained from a Wheatstone bridge. This resistance also gave the temperature of the wire.

For each of the liquids the cooling of wires of two sizes was studied, the diameters being 0.0083 cm. and 0.0155 cm. respectively. Both were thought to be pure platinum, but

Fig. 1.



tests of the resistance at the temperature of melting ice and that of steam gave a very low value for the temperature coefficient of the finer wire.

The apparatus is shown diagrammatically in fig. 1. The platinum wire TT, immersed in the liquid under examination, formed part of the fourth arm of a Wheatstone bridge, having equal ratio arms PP. By adjusting the slider S the



bridge was balanced with a small current (0.01 amp.), thus allowing for slight temperature changes of the fluid. An additional resistance  $dR$  now introduced into the third arm destroyed the balance, which was then restored by increasing the current through the bridge and thus heating the wire TT until its resistance had sufficiently increased. Correction for the cooling at the ends of the test wire was automatically effected by having in the other arm of the bridge a shorter piece 'C' of the same wire \* also immersed in the liquid under examination. To be effective, this compensating wire must be greater than a certain minimum length. Ayrton and Kilgour † have given a calculation showing that for a 6-mil wire at about 300° C. temperature excess in still air, the effect of the heavy leads extends about 1 cm. from each end. For finer wires it would be less, and also it would be less if the cooling medium were a liquid, for these carry off more heat than air, so that the end effects become less important. In the present experiments 'C' was never less than 2 cm., and so the end effect should be entirely eliminated.

The energy dissipated in the uncompensated length ( $l$ ) of TT was calculated from the current ( $i$ ) through the wire and its (hot) resistance  $R$ . The temperature excess ( $\theta$ ) of the wire above its surroundings is given by  $dR/R_0\alpha$ , where  $R_0$  is the resistance of the wire at 0° C. and ' $\alpha$ ' the temperature coefficient of resistance. The heat loss  $H$  (in calories) per cm. length of wire per ° C. temperature excess is given by

$$H = \frac{i^2 R}{4 \cdot 18 l} \div \theta, \quad . \quad . \quad . \quad . \quad (17)$$

where

$$\theta = dR/R_0\alpha,$$

4.18 being the factor required to convert watts to calories per second.

Details of the wires used are given in Table I.

The rectangular vessel containing the liquids under examination had a height of 12 cm. and a base of 17 × 10 cm., and the wires (3 cm. apart) were 3.5 cm. below the surface of the liquid. This vessel required rather larger quantities of some of the liquids than were available. A smaller one was found with carbon tetrachloride to give the same result as the larger, and so it was generally used

\* Callendar introduced this method of eliminating end effects in resistance measurements, using it for many similar purposes. *Proc. Phys. Soc. Lond.* xxxiii. p. 137 (1921).

† Ayrton and Kilgour, *Phil. Trans. A*, clxxxiii. p. 371 (1892).

TABLE I.  
Details of the Wires used.

Diam. <i>d.</i>	$gd^3$ .	Uncompensated length. <i>l.</i>	$\alpha$ .	$R_0$ .
cm. ·0083	$5.62 \times 10^{-4}$	cms. 5.95	·00183	ohms. 2.127
·0155	$36.6 \times 10^{-4}$	6.5	·00385	·355

instead. It was 10 cm. high with a base  $16 \times 6$  cm. It was used quite full and with the wires 5 cm. below the surface of the liquid. In all cases the vessel stood upon an insulated levelling table on a concrete slab on the floor, and no ripples were observable on the liquid surface. It was completely covered in by a draught-proof enclosure of cotton-wool over a cardboard frame, for draughts might by local cooling set up convection currents in the liquid, and might also cause evaporation of the more volatile liquids. A thermometer with  $1/10^\circ \text{C}$ . divisions checked the temperature of the fluid.

Table II. is a summary of the physical constants of the liquids used. It was compiled from published data in books

TABLE II. †  
Physical Constants of the Liquids used.

Liquid.	$10^4k$ .	$10^4a$ .	$\rho$ .	$s$ .	$\eta_T$ .	$cv/k$ .	$ac^2/k^3$	$\eta_{T+25}/\eta_T$ .
Toluene .....	3.42	10.9	0.866	0.40	0.0062	7.24	1118	
Carbon tetra- chloride .....	2.66	11.8	1.582	0.198	0.0108	8.03	1630	.728
Aniline .....	4.1	8.5	1.023	0.514	0.055	69.3	1390	.465
Olive oil.....	3.92	7.0	0.916	0.47	1.17	1402	842	.363
Glycerine .....	6.8	5.3	1.26	0.58	9.3	7940	611	.42*

$s$ =specific heat.  $\eta$ =viscosity.  $\rho$ =density.  $c$ = $sp.$   $v=\eta/\rho$ .

\*  $\eta_{T+10}/\eta_T$ .

of physical constants, and since pure liquids were used it is sufficiently exact for present purposes where (as will be seen later) we are concerned mainly with a small fractional

† The majority of these values were obtained from 'Physical and Chemical Constants, etc.,' by G. W. C. Kaye and T. H. Laby.

power of the values given. Also, as only moderate heating of the wires was involved, little account has been taken of temperature changes of the physical properties of the liquids, though the point is referred to later.

The ratio arms were usually 100 ohms each, 1000 ohms being occasionally used for the larger currents. Equality of the ratio arms was tested by reversing the connexions and noticing whether the balance was thereby disturbed.

To eliminate disturbing resistance changes when the heating current was passed, all connecting wires were compensated by similar wires in the opposite arms of the bridge, and the resistances  $R$  and  $dR$  were constructed of manganin as also was the slide wire  $S$ . It was found on test, by removing the platinum wires  $TT$  and  $CC$  and substituting heavy oil-immersed manganin of the same resistance, that the balance of the bridge obtained with a small current (0.01 amp.) was undisturbed when a heavy current of 1 amp was passed, and that therefore the compensation was satisfactory. A terminal head on the heavy copper leads to the wires facilitated short circuiting of the platinum wires when subsequent occasional test of the apparatus was required.

It was possible that the heating current might set up thermoelectric effects, but a test showed that these were absent. The method was to switch off the heating current after it had been adjusted to the value necessary to balance the bridge, and no appreciable drift of the galvanometer was then observed while the wires were cooling.

Thermoelectric effects might also have existed through local inequalities of temperature caused otherwise than by the heating current, and these would reveal themselves by drift of the galvanometer on making the galvanometer circuit while the battery circuit was still open. Some slight effect was occasionally found, but it was only important when getting the original balance with the small current; and for this it was eliminated by the familiar device of working with the galvanometer circuit always completed and adjusting the bridge for no deflexion when the battery was reversed.

A large storage battery was used at first, and it gave troublesome galvanometer effects due to leakage, discovered and traced by reversal of the battery and galvanometer circuits. To eliminate these a separate 10-volt battery was used, and this and all parts of the apparatus and leads were insulated by standing upon ebonite disks, etc.

The increment resistance  $dR$  was obtained from a box of manganin coils (resistance 0.01 to 1.0 ohm) provided

with mercury cups. A separate test showed that the resistance of the coils was independent of the current. Values of  $dR$  down to 0.001 ohm were obtained by shunting a resistance of 1 ohm by 1000 ohms, etc. These values were calibrated directly on a Cambridge resistance bridge, and agreed with calculation. Using a current of 0.01 ampere through the bridge it was possible to obtain the initial balance correct to 0.0001 ohm, or rather less, an amount associated with a galvanometer deflexion of  $2/5$  mm. on reversal of battery. Thus, with a possible error of setting of 0.0001 ohm, values of  $dR=0.1$  would be correct to  $1/10$  of one per cent., and generally the error would be negligible, but with the smallest values of  $dR$  used (0.001 ohm) the error might be between 5 and 10 per cent., and averages were taken. With the heating current, of course, the bridge was much more sensitive. With the 3-mil wire and a current of  $\frac{1}{2}$  amp. a resistance change of 0.0001 ohm in the third arm would cause a galvanometer deflexion of 1 cm. Incidentally it was noticed that a change of 1 per cent. in this current value caused a deflexion of 13 cm., and this was also approximately the case with the larger wire.

As a further check on the apparatus, the cooling in gases was studied by a volt-drop method instead of using the Wheatstone bridge arrangement. Various experimenters have used this method, measuring the current through a given length of wire and the volt drop along it. To minimize end effects, experimenters have usually used potential leads of very fine wire, attached at sufficient distances from the heavy current leads to eliminate the cooling effects of these latter. This, however, does not eliminate whatever cooling is due to the fine potential leads, and the volt-drop method used in the present experiments is superior in this respect. The method was to pass the current through TT and CC in series, and to measure the respective potential falls by means of a potentiometer. The difference gave the potential drop along the uncompensated length, the end effects being eliminated completely. The current was obtained by passing it also through a standard manganin resistance and determining the volt drop for this also. The resistance TT-CC at the temperature of the air was obtained from the potential drop when a very small current 0.01 amp. was passing. The results obtained by this check method were within 1 or 2 per cent. of those obtained by means of the Wheatstone bridge. It is not so convenient a method for the liquids, owing to the zero changes which are easily dealt with by the Wheatstone bridge method.



*Experimental Observations.*

Certain general characteristic effects were noticed during the experiments.

With slight heating of the wire the conditions ultimately set up were usually quite steady, except perhaps for a slight drift with the more viscous liquids due to the fact that the prolonged heating necessary before the steady state was reached gradually increased the temperature of the whole mass of the fluid. However, with greater heating, unsteadiness supervened, the galvanometer deflexion and also the current changing spasmodically, as though the convection current had become turbulent or reached some critical condition.

Various measurements were made of the drift mentioned, which was found to be of the order expected from the known energy dissipation in the volume of liquid used. Observations were taken while a heating current was passing, sometimes of the decrease of current necessary as time elapsed to keep the temperature of the wire constant, and sometimes, with constant current, of the ultimate rate of temperature rise of the wire. Observations were also taken of the resistance of the cold wire just before the heating current was passed, and again at such a time after switching off that all local heating of the liquid had been dissipated. In the case of glycerine this dissipation occupied some minutes, and a true drift of 0.001 ohm during an experiment appeared as great as 0.01 ohm when taken too soon after switching off. Results were satisfactorily consistent, and in general were equivalent to a change in  $\theta$  of the order of one quarter of one per cent. per minute. The less viscous fluids attained the steady state too quickly for this drift to have appreciable effect.

Another effect was noticed with the more viscous liquids. For instance, with the 5-mil wire immersed in olive oil slight heating currents gave a tendency for the galvanometer to drift in a certain direction as though the whole mass were being gradually heated up. With greater heating, however, an opposite drift was observed. This was found to be due to oscillations having a period of a minute or so, which slowly died out and left the usual steady state. Thus, while on switching on a very slight heating current the wire merely rose gradually in temperature to its final value ( $2^{\circ}$  C. excess), reaching this in about three minutes, it was found that for rather greater heating ( $5^{\circ}$  C.) the temperature of the wire first overshot its final value by about  $1/8^{\circ}$  C., reaching a maximum in about one minute, and then fell gradually to its steady state. With



still greater heating ( $10^{\circ}\text{C.}$ ) two oscillations were noticed, a maximum being reached in  $\frac{1}{2}$  minute followed by a minimum  $\frac{3}{4}$  minute later, from which the temperature then rose to its final value. These oscillations resemble those of a damped system, the three stages due to different degrees of heating corresponding to three different degrees of damping. The phenomena cannot be attributed to the galvanometer, and must have their origin in the liquid convection currents set up, for the galvanometer normally reached its final deflexion in a few seconds, whereas the observed variations occupied minutes.

### Results.

The results obtained are given below in tables compiled from smooth curves through experimental points, this making it possible to give them much more concisely than would otherwise have been the case.

It is necessary to state that, in general, results were reproducible to within 5 per cent. With respect to reproducibility, the glycerine series was least satisfactory, but this may have been due to its extremely viscous nature and to the very rapid manner in which its viscosity changes with temperature.

In Table III. results are given for the various liquids,

TABLE III.

Relation between  $10^4H$  and  $\theta$ .

[Heat loss ( $H$ ) in calories per cm. length per  $^{\circ}\text{C.}$  excess temperature.]

Liquid.	Wire diam.	$g$ <i>cal/cm.k.</i>	Temperature excess ( $\theta$ ) $^{\circ}\text{C.}$					
			1.	2.	5.	10.	20.	50.
Gases* .....	0.0083	$4.74 \times 10^{-5}$		0.82	0.83	0.86	0.91	1.03
	0.0155	$3.09 \times 10^{-4}$			0.99	1.03	1.10	1.23
Toluene.....	0.0083	0.624		8.6	9.5	10.4	11.1	12.6
	0.0155	4.06	9.8	10.7	12.1	13.6	15.4	18.2
$\text{CCl}_4$ .....	0.0083	0.920	6.3	6.8	7.7	8.4	9.2	10.3
	0.0155	5.98	8.1	9.1	10.5	11.7	12.9	14.9
Aniline .....	0.0083	0.782	7.5	8.4	9.6	10.8	12.1	14.6
	0.0155	5.08	9.9	11.0	12.3	14.1	16.2	19.4
Olive oil ...	0.0083	0.472		5.3	6.1	6.7	7.4	8.6
	0.0155	3.08		6.8	7.6	8.7	9.9	12.0
Glycerine ...	0.0083	0.343		9.6	9.4	9.5	10.3	
	0.0155	2.23		9.9	10.7	11.9	13.5	16.2

\* For gases  $\theta$  was varied up to  $200^{\circ}\text{C.}$ , and the values of  $10^4H$  obtained for the two wires at  $\theta=200^{\circ}\text{C.}$  were 1.34 and 1.60 respectively.

showing the relation between the linear emissivity  $H$  of the wire in cal. per cm. length per degree temperature excess, and the temperature excess  $\theta$ .

(a) *Representation in the form*  $H/k = F(c^2gd^3a\theta/k^2)f(cv, k)$ .

In Table IV. these results are represented in the form showing the relation to the equation for inviscid fluids, and  $H/k$  is given for various values of  $(c^2gd^3a\theta/k^2)$ , the value of  $cv/k$  for the liquid being stated. The heat losses obtained for air do not appear in this table as they fall under very much smaller values of  $(gd^3a\theta c^2/k^2)$ .

TABLE IV.  
Relation between  $H/k$  and  $gd^3ac^2\theta/k^2$ .

Liquid.	$cv/k$ .	Wire diam.	$gd^3ac^2\theta/k^2$ .							
			1.	2.	5.	10.	20.	50.	100.	200.
Toluene.....	7.2	0.0083	2.5	2.6	3.0	3.2	3.5	4.1	4.7	
		0.0155			2.9	3.2	3.6	4.1	4.6	
CCl <sub>4</sub> .....	8.0	0.0083	2.3	2.6	2.9	3.2	3.5	4.0		
		0.0155				3.2	3.6	4.2	4.7	5.2
Aniline .....	69	0.0083	1.9	2.2	2.5	2.8	3.2	3.8	4.3	
		0.0155			2.5	2.7	3.0	3.5	4.0	4.6
Olive oil ...	1400	0.0083	1.4	1.6	1.8	2.0	2.1			
		0.0155			1.7	1.9	2.1	2.4	2.8	3.3
Glycerine...	7640	0.0083	1.4	1.4	1.5	1.7				
		0.0155			1.4	1.5	1.7	2.0	2.4	

It is clear from the table that for a given liquid the relation between  $H/k$  and  $c^2gd^3a\theta/k^2$  is practically independent of the diameter of the wire.

There appears, however, to be a tendency for the finer wire to give values of  $H/k$  a few per cent. higher than the other, and this is most probably due to the temperature variation of the properties of the fluids for which no allowance has been made.

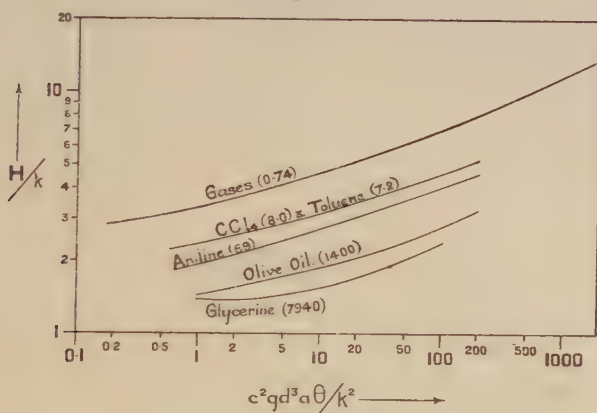
In considering the cooling of the wires in gases, where much greater temperature excesses were involved, it was found that approximate allowance of this kind corrected a similar tendency\*. It appears on approximate calculation from what data are available (mainly temperature coefficients of viscosity) that in the present experiments the

\* Davis, Phil. Mag. xliii. p. 329 (1922).

correction to be expected is sensible, and is of the sign and order of magnitude required to bring the results for the two wires into even closer agreement. In fig. 2 single curves have been drawn representing mean values for each of the liquids.

Although our own figures for gases fall on a very distant region of the graph and so are not shown, a curve has been given to represent gases. It was obtained from the paper already mentioned, where cooling was studied for a wide range of wire diameter and of temperature excess, for various gases—oxygen, hydrogen, and air—over a thousand-fold range of gas-pressure.

Fig. 2.



It is seen that the curves for the different fluids form a family of more or less parallel lines, with  $cv/k$  as parameter. The magnitude of the effect of  $cv/k$  is not great, for although glycerine has a value more than 10,000 times that for air, the value of  $H/k$  for a given value of  $c^2gd^3a\theta/k^2$  is only reduced in the ratio 3:1. It is satisfactory that toluene and carbon tetrachloride, with values of  $cv/k$  so nearly the same, should be represented by one line. The curve for diatomic gases ( $cv/k=0.74$ ) may be shown to agree with published results for cooling of wires in  $\text{CO}_2$  ( $cv/k=0.83$ ), so that here again it appears that  $cv/k$  determines the position of the curve.

A logarithmic plot of the relation between  $H/k$  and  $cv/k$  for various constant values (1, 10, and 100) of  $c^2gd^3a\theta/k^2$  yields more or less linear relations; and it appears that within

the limits of our experiments the complete equation for the cooling of wires in fluids is given by

$$H/k \propto (c^2 g d^3 a \theta / k^2)^x (c\nu/k)^{-y}, \quad . \quad . \quad . \quad (18)$$

where  $x$  varies from  $1/10$  to  $1/6$

and  $y$  varies from  $1/10$  to  $1/8$ .

It is noticed that  $x$  and  $y$  have nearly equal values, and if we put  $x=y$ , equation (6) becomes

$$H/k \propto (d^3 \theta g a c / k \nu)^x, \quad . \quad . \quad . \quad . \quad (19)$$

which is in agreement with the theoretical equation (16). There appears to be no published evidence to show whether this simplified grouping is of more general applicability, but in this connexion it is interesting to note that Lorenz, in calculating the convective cooling of a vertical plate in a viscous gas, obtained a result reducible to this form. The assumptions he made led in his special case to the result represented by  $x=y=1/4$ . This index is rather higher than those given above, but it is known from an extended curve for gases that for larger cylinders  $x$  tends to increase to a value of  $1/3$ .

(b) *Representation of results in the form  $H/k = F(d^3 \theta g a c / k \nu)$ .*

We now proceed to show graphically the extent to which the present experimental results agree with this theoretical equation.

If satisfactory, results plotted with  $H/k$  as ordinate and  $(d^3 \theta g a c / k \nu)$  as abscissa should yield one line independent of the nature of the liquid used. Strictly it is necessary to make allowance for the temperature change in the physical properties of the liquids. Unfortunately, reliable data do not seem to be available for some of the properties, but it appears that the viscosity provides the most rapid change, and its temperature coefficient is usually known.

Consequently, while in this paper temperature variations in the other variables are neglected, an attempt will be made to allow for them in the case of viscosity. As a first approximation, the value taken for the viscosity in any experiment is that appropriate to a temperature intermediate between the temperature of the hot wire and that of the main volume of cold liquid in which it is immersed. If the cooling wire is  $50^\circ \text{C.}$  hotter than the cold liquid, the viscosity taken is that for a temperature  $25^\circ \text{C.}$  in excess of that of

the liquid. The factor  $\eta_{T+25}/\eta_T$  is given in Table II. and it is seen that the temperature change is considerable, particularly with glycerine.

From results obtained, and using the above correction for temperature changes in viscosity, Table V. and fig. 3 have been derived, and each liquid is represented on the graph by four points. The extreme points of each set refer to the extremities of the range of the experimental results. They refer respectively to the cooling of the fine wire at 2° C. excess and that of the other wire at 50° C. excess.

TABLE V.

Relation between  $H/k$  and  $gd^3a\theta c/k\nu$ .

Fluid.	Wire diam.	2° C. excess.		50° C. excess.	
		$gd^3a\theta c/k\nu$ .	$H/k$ .	$gd^3a\theta c/k\nu$ .	$H/k$ .
Air† .....	0.0083	0.120	1.41	0.235	1.66
	0.0155	0.83		0.153	1.99
CCl <sub>4</sub> .....	0.0083	0.229	2.55	7.90	3.86
	0.0155	1.49	3.42	51.3	5.62
Aniline .....	0.0083	0.225	2.04	1.21	3.56
	0.0155	1.47	2.61	7.9	4.74
Olive oil .....	0.0083	0.367	1.34	0.47	2.18
	0.0155	0.44	1.73	0.30	3.07
Glycerine .....	0.0083	0.87	1.18	0.21*	1.51*
	0.0155	0.56	1.44	0.134*	1.99*

\* These refer to  $\theta=20^\circ\text{C}$

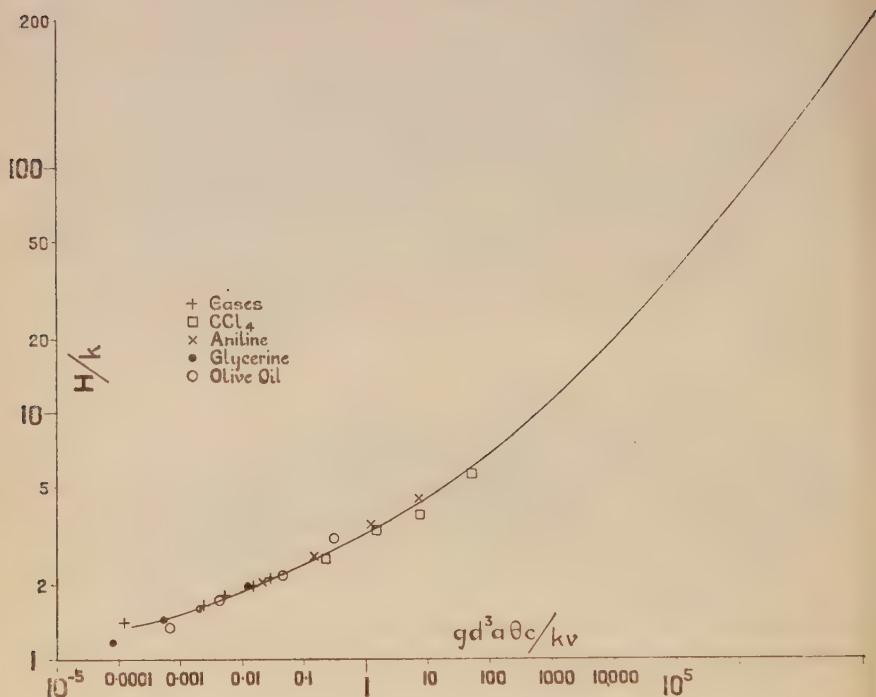
† On the graph of fig. 3 are also plotted the following values for the wires at 200° C. excess in air:—

Wire diam. ...	0.0083	0.0155
$gd^3a\theta c/k\nu$ .....	$5.12 \times 10^{-3}$	$3.00 \times 10^{-2}$
$H/k$ .....	1.81	2.14

It is seen that the points all lie very well on one curve, so that equation (16) appears to represent the results of the present experiments very satisfactorily. The upward extension of the curve beyond the points plotted is the representation on the present basis of the upper part of the curve for gases already referred to.



Fig. 3.



### *The Cooling Power of Fluids.*

It appears from the theoretical considerations and experimental evidence put forward in this paper and previously, that the convective cooling of similar bodies immersed in fluids may be represented by the formula

$$hL/k\theta = F(c^2 g L^3 a \theta / k^2) f(c\nu/k),$$

and the form of the function  $f(c\nu/k)$  is now indicated to be such that we may write the simpler expression

$$hL/k\theta = F(L^3 g a c / kv).$$

It is to be expected that such a grouping of variables is of more general applicability than for the special case of infinite fluids, especially in so far as it can be obtained from the Principle of Similitude. Where liquids by their natural convective motion carry heat from a hot surface and yield it to a cold one, as with the common case of a hot body immersed in a fluid contained in a cooler vessel, one would in general expect approximate agreement with the formula

if  $\theta$  represented the temperature difference between the two surfaces. A few experiments would soon test the applicability in any doubtful case.

For any circumstances to which the formula applies, the form of the function  $F$  may be obtained from an experiment in which only one of the variables (say  $\theta$ ) is altered. We have some knowledge of its form in certain cases. For cooling of large bodies in free air or in enclosures, large compared with the size of the cooling body, we may write

$$hL/k\theta \propto (L^3\theta g\alpha c/k\nu)^n,$$

where  $n$  is usually about  $1/4$ , but tends to be as great as  $1/3$  for large bodies or very hot ones, and to be much smaller for fine wires only slightly heated, as in the present experiments. Measurements of the conductivity of fluids have been made by methods involving fine wires very slightly heated along the axis of a small metal tube: the validity of this method implies that  $n=0$  in this extreme case.

Since for a given set of circumstances the value of  $n$  depends upon the size of the model and upon its temperature excess, it is obvious that the cooling power of a fluid depends upon the circumstances in which it is to be used. Retaining from the above formula only those quantities which relate to the properties of the cooling fluid, we have

$$h \propto k(ac/k\nu)^n,$$

and for the conditions so far studied  $n$  varies from 0 to  $1/3$ , so that the relative cooling power of a fluid may vary between the limits

$$k \text{ and } (ack^2/\nu)^{\frac{1}{3}}.$$

Thus it appears for these conditions that the conductivity of the fluid is the preponderating physical property determining cooling power. This result is probably fairly general, for while it may be possible to devise experimental arrangements in which  $k$  does not enter, suitable conditions for its omission seem generally unlikely to be realized, for it evidently enters vitally whenever the temperature of a particle of fluid (and thus the vigour of its motion and the amount of heat it absorbs or yields) depends upon the thermal conductivity of the adjacent layers.

The effect of the physical properties, other than thermal conductivity, appears to be such that high specific heat and high coefficient of expansion have the same degree of importance in facilitating cooling that high viscosity has in restricting it.

I desire to express my thanks to Dr. G. W. C. Kaye and Dr. Elzer Griffiths for the kind and encouraging way in which the facilities for the present work have been provided, to Mr. W. G. Bickley, M.Sc., for critically reading a draft of the theoretical part, and to my wife for assistance with the numerous calculations involved in the reduction of the experimental observations.

May 1922.

LXXX. *The Cooling Power of a Stream of Viscous Fluid.*  
By A. H. DAVIS, M.Sc.\*

[From the National Physical Laboratory.]

IN some previous papers† the author has studied the phenomenon of convective cooling, both natural and forced, from the point of view of similitude, and has shown how excellently experimental data for gases agree with a grouping of variables that Boussinesq‡ deduced by hydrodynamical reasoning for inviscid fluids. The most recent § of this series of papers considered for *natural* convective cooling the necessary modifications of Boussinesq's analysis in dealing with the problems of viscous fluids, and the new formula thus obtained was tested experimentally in certain conditions and found to be satisfactory.

The present note develops the theory of *forced* convection in the same way, studying the effect of introducing a viscosity term into Boussinesq's analysis for inviscid fluids.

The problem concerns the cooling of a hot body immersed in an infinite fluid stream maintained at a certain temperature,  $\theta$  degrees in excess of that of the fluid at infinite distance to which all temperatures are referred. The fluid stream is rectilinear, and moving with uniform velocity  $v_{\infty}$  at distances from the body sufficiently great. This velocity is supposed to be sufficiently great for the natural convection (gravity) currents set up by the hot body itself to be negligible. We thus neglect the coefficient of expansion of the liquid.

Let  $\rho$  and  $\nu$  be respectively the density of the fluid and its kinematical viscosity. At a given time  $t$ , and for an element of the fluid at the point  $x, y, z$ , let  $\tau, u, v, w, P$  be the

\* Communicated by the Author.

† Phil. Mag. xl. p. 691; xli. p. 899; xliii. p. 329.

‡ Boussinesq, *Comptes Rendus*, cxxxii. p. 1382; cxxxiii. p. 257 (1901).

§ See p. 920.

temperature excess, the three components of its velocity, and the non-hydrostatic part of its pressure. If  $l, m, n$ , are three direction cosines of the general stream of velocity " $v_\infty$ ," we have as boundary conditions :

$$\left. \begin{array}{l} \text{At infinite distance from} \\ \text{the origin} \end{array} \right\} \begin{array}{l} u, v, w = v_\infty (l, m, n), \\ (P, \tau) = 0. \end{array} \quad \left. \begin{array}{l} \text{At the surface of the solid} \\ (u, v, w) = 0, \quad \tau = \theta. \end{array} \right\} \quad (1)$$

The hydrodynamical equations of continuity and of motion are

$$\left. \begin{array}{l} \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0, \quad \frac{1}{\rho} \frac{\partial P}{\partial x} = -u' + \nu \nabla^2 u, \\ \frac{1}{\rho} \frac{\partial P}{\partial y} = -v' + \nu \nabla^2 v, \quad \frac{1}{\rho} \frac{\partial P}{\partial z} = -w' + \nu \nabla^2 w \end{array} \right\} \quad (2)$$

$u', v',$  and  $w'$  being the accelerations of the fluid parallel to the axes.

Let  $k$  be the thermal conductivity of the fluid and  $c$  its heat capacity per unit volume, then  $\tau'$ , the rate of change of temperature for a given particle with respect to time, is given by

$$\tau' = (k/c) \nabla^2 \tau \quad (3)$$

Also we have

$$\begin{aligned} u', v', w', \tau' = u \frac{\partial(u, v, w, \tau)}{\partial x} + v \frac{\partial(u, v, w, \tau)}{\partial y} \\ + w \frac{\partial(u, v, w, \tau)}{\partial z} + \frac{\partial(u, v, w, \tau)}{\partial t}. \end{aligned} \quad (4)$$

The equations in  $P, u, v, w$  are everywhere quite separate from those in  $\theta$ , and hydrodynamically the problem is the same as that where  $\theta=0$ , the motion of the fluid being determined entirely by the given general stream and the configuration of the immersed body. Everywhere  $u, v,$  and  $w$  will be proportional to  $v_\infty$ , and  $P$  proportional to  $\rho v_\infty^2$ .

Let us endeavour to replace the independent variables  $t, x, y, z$  and the functions  $\tau, u, v, w, P$  by others  $t_1, \xi, \eta, \zeta, T, U, V, W, \Pi$  respectively proportional to them but whose ratios are chosen to eliminate  $\theta, k/c, \rho, \nu, v_\infty$ .

Let us consider the following substitutions :

$$\left. \begin{array}{l} \xi, \eta, \zeta = (v_\infty/\nu)(x, y, z), \quad (u, v, w) = v_\infty (U, V, W), \\ \tau = \theta T, \quad P = \rho v_\infty^2 \Pi, \quad t = (\nu/v_\infty^2)t_1. \end{array} \right\} \quad (5)$$

It is readily found that the substitutions effect the eliminations satisfactorily if  $cv/k=1$ . For gases  $cv/k$  is approximately equal to unity, and the substitutions should be satisfactory on this ground. Also they are satisfactory if the accelerations  $u' v' w'$  of the particle are negligible compared with  $\nu \nabla^2 u$ , etc., as would appear justifiable for very viscous fluids.

In either of these circumstances the equations take the form ( $U' V' W'$  being omitted unless  $cv/k=1$ ):

$$\left. \begin{aligned} \frac{\partial U}{\partial \xi} + \frac{\partial V}{\partial \eta} + \frac{\partial W}{\partial \zeta} &= 0, & T' &= \frac{\partial^2 T}{\partial \xi^2} + \frac{\partial^2 T}{\partial \eta^2} + \frac{\partial^2 T}{\partial \zeta^2}, \\ \frac{\partial \Pi}{\partial \xi} &= -U' + \left( \frac{\partial^2 U}{\partial \xi^2} + \frac{\partial^2 U}{\partial \eta^2} + \frac{\partial^2 U}{\partial \zeta^2} \right), \\ \frac{\partial \Pi}{\partial \eta} &= -V' + \left( \frac{\partial^2 V}{\partial \xi^2} + \frac{\partial^2 V}{\partial \eta^2} + \frac{\partial^2 V}{\partial \zeta^2} \right), \\ \frac{\partial \Pi}{\partial \zeta} &= -W' + \left( \frac{\partial^2 W}{\partial \xi^2} + \frac{\partial^2 W}{\partial \eta^2} + \frac{\partial^2 W}{\partial \zeta^2} \right), \end{aligned} \right\} \quad (6)$$

where

$$\begin{aligned} (U', V', W', T') &= U \frac{\partial(U, V, W, T)}{\partial \xi} + V \frac{\partial(U, V, W, T)}{\partial \eta} \\ &\quad + W \frac{\partial(U, V, W, T)}{\partial \zeta} + \frac{\partial(U, V, W, T)}{\partial t_1}. \end{aligned}$$

Let us put the equation of the solid in the form

$$f[(v_\infty/\nu)(x, y, z)] = 0. \quad (7)$$

Thus, if  $v_\infty/\nu$  changes, this amounts to considering instead of the actual solid, similar bodies having linear dimensions inversely proportional to  $v_\infty/\nu$ . The direction cosines  $l, m, n$  of the normal will remain the same at corresponding points, and the boundary conditions become :

$$\left. \begin{aligned} \text{At the surface} \quad U &= V = W = 0, & T &= 1, \\ \text{At the distance } \sqrt{\xi^2 + \eta^2 + \zeta^2} &\text{ infinite} \quad U &= l, \quad V &= m, \quad W &= n. \end{aligned} \right\} \quad (8)$$

The system of equations (6) and (8) determine  $U V W \Pi T$  as functions of  $\xi, \eta, \zeta$ , and  $t_1$ , and substituting in the integrals for the new variables their equivalents, we obtain

$$\left. \begin{aligned} \frac{\tau}{\theta} \frac{u, v, w}{c}, \frac{P}{\rho c}, z &= \text{definite functions of} \\ &[(v_\infty/\nu)(x, y, z); v_\infty^2 t/\nu]. \end{aligned} \right\} \quad (9)$$



The flux of heat  $h$  furnished in unit time by unit area of such a body, equal to that which the contiguous fluid layer communicates to the interior of the fluid, is given by

$$k \left( l_1 \frac{\partial \tau}{\partial x} + m_1 \frac{\partial \tau}{\partial y} + n_1 \frac{\partial \tau}{\partial z} \right). \quad . \quad . \quad . \quad (10)$$

Introducing the new variables, we have

$$h = (k c_x \theta \nu) \left( l_1 \frac{\partial T}{\partial \xi} + m_1 \frac{\partial T}{\partial \eta} + n_1 \frac{\partial T}{\partial \zeta} \right). \quad . \quad . \quad (11)$$

At corresponding points of the surfaces  $f(\xi, \eta, \zeta) = 0$  limiting the bodies considered, the direction cosines  $l_1, m_1, n_1$  have the same values, and at corresponding times  $t_1 = \text{const.}$  the derivatives  $\frac{\partial T}{\partial (\xi, \eta, \zeta)}$  at corresponding points have also the same values. Consequently, at corresponding times the trinomial coefficient is a function of the shape and orientation of the bodies only.

Thus, for a family of similar bodies similarly orientated, having linear dimensions  $L$  given by

$$L \propto \nu / v_\infty, \quad \text{i.e. } v_\infty L / \nu = \text{const.}, \quad . \quad . \quad . \quad (12)$$

the heat loss per unit area at corresponding times from corresponding points is given by

$$h \propto k \nu \theta / \nu; \quad . \quad . \quad . \quad . \quad (13)$$

and this will also be true if " $h$ " be the mean heat loss taken at the given instant over the whole surface of the solid.

So for bodies of this shape and orientation we have

$$h = (k v_\infty \theta / \nu) f \{ v_\infty L / \nu; v_\infty^2 t / \nu \}, \quad . \quad . \quad . \quad (14)$$

which may be written

$$\frac{hL}{k\theta} = F \left\{ \frac{v_\infty L}{\nu}; \frac{v_\infty^2 t}{\nu} \right\} \quad . \quad . \quad . \quad . \quad (15)$$

When the conditions have become steady—that is, independent of time  $t$ ,—the formula reduces to

$$\frac{hL}{k\theta} = F \left( \frac{v_\infty L}{\nu} \right). \quad . \quad . \quad . \quad . \quad (16)$$

And, further, if the conditions do not settle down to complete steadiness, but settle down to periodic fluctuations, then these fluctuations will be similar in form for corresponding cases, and the average value of the heat loss will still be given by (16).

It is desirable to recall two alternative conditions which have been introduced into the proof of the formula. They are that  $cv/k$  shall be equal to unity or else very large. If these conditions are not satisfied, it may be shown that the formula becomes

$$\frac{hL}{k\theta} = F\left(\frac{v_{\infty}L}{\nu}; \frac{cv}{k}\right), \dots \dots \dots (17)$$

where  $cv/k$  is expected to be of little importance in the two extreme cases mentioned.

Whether the simpler formula is true for gases on the one hand and for very viscous fluids on the other, and whether  $cv/k$  is important for intermediate circumstances, is a matter for experimental investigation. From data already available it is known that the simpler form is fairly satisfactory for gases, being indistinguishable in this case from the grouping of variables deduced by Boussinesq for inviscid fluids. This is shown graphically in a curve between  $hL/k\theta$  and  $v_{\infty}L/\nu$ , given elsewhere\*, for the cooling of wires in a stream of air ( $H/k$  and  $vl/\nu$  in the notation of the actual graph). Corresponding data for liquids are not yet available, but an isolated result has been given by Worthington and Malone† for the cooling of a wire in water ( $cv/k=7$ ;  $\nu=0.01006$ ), and this yields a result,  $H/k=21.6$ ,  $vl/\nu=38$ , which is in satisfactory accord with the curve mentioned for air. In the analogous case of *natural* convection,  $cv/k$  has been shown to be of little importance for a wide range of viscous fluids.

July 1922.

LXXXI. *A Sodium-Potassium Vapour Arc Lamp.* By F. H. NEWMAN, D.Sc., A.R.C.S., Head of the Physics Department, University College, Exeter‡.

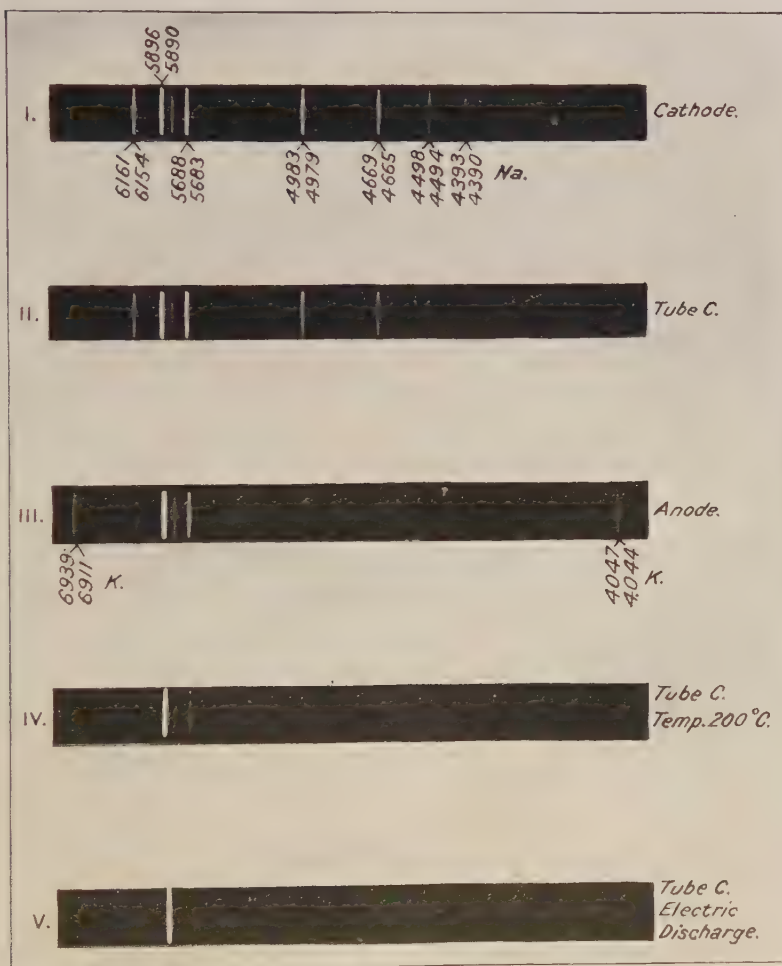
[Plate V.]

METALLIC arcs operated in vacua give very intense radiation, and the lines in the resulting spectra are very narrow, whereas with a substance placed between the poles of a carbon arc, working under ordinary conditions, broad lines are obtained, which often show much reversal, the centres of the lines being comparatively faint. This is the case when the sodium D lines are excited, and a bunsen flame, to which salt has been added, is not a suitable source of sodium radiation. As the amount of salt is increased, the

\* Phil. Mag. xli, p. 899 (1921).

† Journ. Frank. Inst. clxxxiv, p. 115 (1917).

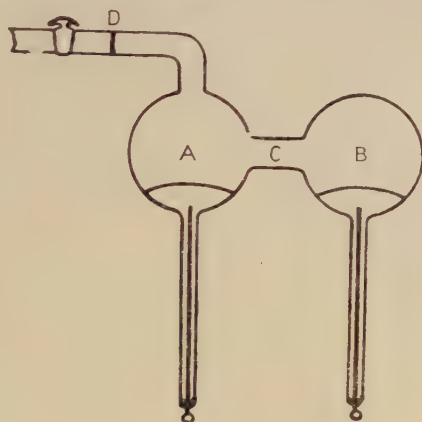
‡ Communicated by the Author.





lines are broadened and show much reversal. Modern practical and research needs require intense radiation and a monochromatic source. The chief line must be sufficiently removed from its immediate neighbours, so that if a relatively wide slit is used, other wave-lengths in the immediate vicinity of the one desired are excluded. The quartz-mercury vapour lamp provides such a source; it is easy to construct and work, and does not require continuous pumping to keep it exhausted while running. A sodium vapour arc lamp, working on the same principle, has been designed and constructed by Rayleigh\*, but it is more difficult to work than the mercury lamp. Iron electrodes are unsuitable, since they fuse and drop off after the lamp has been in use for an hour or two. Tungsten, which seems to withstand the action of sodium vapour, is used instead of iron. This

Fig. 1.



lamp requires an applied potential difference of 200 volts when working, although the actual drop of potential across the arc is very much less. The author† has used, previously, a sodium vapour electric discharge-tube which gives intense sodium radiation, but requires continuous heating while the electric discharge is passing. The sodium-potassium vapour arc lamp described in the present work needs no applied heat, can be worked with a small applied potential difference, and requires no attention while it is running.

The form of lamp is shown in fig. 1. It is made of quartz, the bulbs A, B being about 3 cm. in diameter, and joined by a piece of quartz tubing C of internal bore 5 mm. and length

\* Hon. R. J. Strutt, Proc. Roy. Soc., A. xvi. (1919).

† Proc. Phys. Soc. xxxiii. pt. ii. (1921).



15 mm. The electrodes are iron rods 4 mm. in diameter, and are sealed with sealing-wax. The current used must be such that these rods never become so hot that the wax is melted or softened. The liquid alloy of sodium and potassium—two parts by weight of sodium and one of potassium—is run into the bulb A, and the exit tube D then connected to a glass tap, and the whole exhausted. The lamp can then be disconnected from the pump. An electric discharge is passed through the lamp, the alloy being made the cathode. Under the action of the discharge the oxide on the surface of the alloy disintegrates, and the surface becomes quite clean. Tilting the lamp, some of the alloy flows into the other bulb B. Using this method of introducing the alloy, the part C remains quite free from the alloy. With direct current the lamp works with a minimum applied potential difference of 30 volts, although when once the arc is struck, the fall of potential is only 10 volts with a current of 1.5 amps. The arc is struck either by tilting the lamp in the same way that the mercury lamp is started, or one terminal is connected to a small induction coil and a momentary discharge passed. No external heat is required, as that produced by the current is sufficient to vaporize the sodium and potassium. As the temperature rises the current decreases, and the potential difference across the terminals becomes greater. With currents smaller than 2.5 amps. the temperature of the quartz at C is never such that a piece of paper held at this part is charred, and the wax seals do not soften, however long the lamp is working. There is no "browning" of the silica. As the applied potential difference is increased, the radiation becomes brighter, and greater luminosity can be obtained by warming the part C with a small gas flame. This part of the apparatus is, of course, hotter than the other parts, owing to the high current density. The lamp works satisfactorily at any potential between 30 and 200 volts, and the current can be regulated by a resistance in series. If the current rises above 2.5 amps, there is the characteristic "browning" of the silica. The lamp does not require continuous pumping while it is working. The sodium-potassium alloy absorbs all gases, particularly nitrogen and hydrogen, while the current is passing. In this manner a very good vacuum is maintained, however long the lamp is in operation. This fact, and the low voltage at which the arc is struck, are two important improvements on the other forms of sodium vapour lamp. The present form will not work satisfactorily with alternating currents.

With the lamp it was found that the potassium lines were

very faint compared with the sodium lines under all conditions, and they became weaker as the temperature increased. The relative brightness of the sodium and potassium lines differed in various parts of the lamp, and the subordinate series lines of sodium varied in intensity compared with the D lines, although the latter were always the brightest. At the cathode the potassium lines were very weak, while the subordinate series lines of sodium were strong (Pl. V. fig. i.) At C the radiation was very intense (Pl. V. fig. ii.), while at the anode the potassium lines were brighter than they were at other parts of the lamp (Pl. V. fig. iii.). The spectrograms were photographed with a constant deviation type of spectrometer. Wratten panchromatic plates being used. The subordinate series lines of sodium became faint when the current was reduced, and when the lamp was heated externally (Pl. V. fig. iv.). The electric discharge gave a radiation consisting almost entirely of the D lines (Pl. V. fig. v.).

The intensity of the spectrum lines emitted by a mixture of vapours when subject to electrical stimulus depends on the ionization and resonance potentials of the various vapours, and also on the partial vapour pressures. On the Bohr theory the spectrum lines have their origin in the movements of an electron within the atom when it moves from one temporary orbit to another. In the case of sodium the innermost orbit is that represented by the limit of the principal series—that is, by the term  $1.5S$ . The second orbit is represented by the term  $2p$ , and the frequency of the resonance line is that of the first principal line  $1.5S - 2p$ . The theoretical value of the resonance potential of sodium vapour is 2.10 volts, and electrons of this energy produce the D lines. Electrons having a velocity corresponding to about 5.13 volts are able to ionize sodium vapour and cause it to emit all the lines, including those of the subordinate series. The resonance potential of potassium vapour is 1.60 volts, while the ionization potential is 4.33 volts. In a mixture of sodium and potassium vapours, as the accelerating potential is increased, the 7699, 7665 doublet of potassium should appear first, then the 5896, 5890 doublet of sodium, followed by the subordinate series of potassium and sodium respectively. The doublet 7699, 7665 being near the limit of the visible spectrum would be faint, and so it is to be expected that the D lines will, under all conditions, be the brightest lines in the spectra.

When the current density is increased, the subordinate series lines increase in luminosity. Sodium vapour having only one resonance potential, the elevation in energy of the

electrons colliding inelastically must be produced by successive impacts or by absorption of radiation of suitable frequency. The electron normally in the  $1.5\text{ S}$  orbit of the sodium atom may be forced into the  $2p$  orbit by direct impact. It is possible, however, that the ejection may be brought about by absorption of radiation of frequency  $1.5\text{ S}-2p$ . Before it is able to return to the  $1.5\text{ S}$  orbit and emit this radiation, collision occurs with a second electron, and the electron within the atom is ejected to an orbit still farther removed from the innermost stable orbit. It then returns to the  $1.5\text{ S}$  orbit in two stages, the first step causing the emission of a line in the subordinate series, the second step giving the D lines. The chances of this type of collision occurring will increase as the density of the free electrons becomes greater. This also explains why the subordinate series lines are very faint compared with the D lines when an electric discharge is sent through the lamp, for the current density in this case is comparatively small.

LXXXII. *The Protection of Brass Weights.* By J. J. MANLEY, M.A., *Research Fellow, Magdalen College, Oxford*.\*

SIXTEEN years ago, I applied to a set of brass weights a method introduced by Faraday for protecting iron from rust; and as the experiment has been highly successful, other workers may find the plan, or a modification of it described below, helpful.

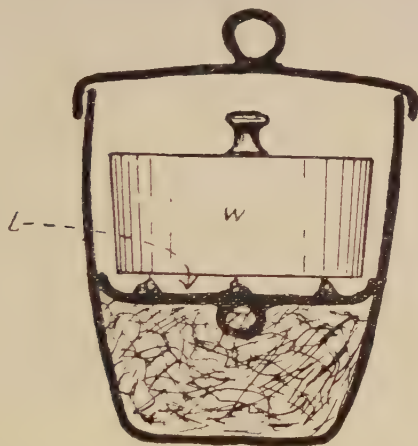
The weights, some of them badly corroded, were first lightly tooled and then suitably polished; next they were heated in a semi-luminous gas flame until they were nearly red hot, and then suddenly plunged into boiled linseed oil, wherein they were left to cool. The weights having been removed from the oil, were washed with turpentine and then polished with old linen; subsequently they were adjusted, standardized, and set apart for the use of students beginning their course of Quantitative Chemistry. Now, although the weights have been in regular use throughout the 16 years that have since elapsed, and have been subjected to what may be rightly termed the severest test of laboratory conditions and usage, numerous re-standardizations, the most recent of which was carried out a few weeks ago, have conclusively shown that Faraday's method for the protection of iron is also remarkably effective when applied to brass, and

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as a result I find that the original relative values of the whole set of weights are still retained; no re-adjustment has been required. These observations and conclusions are also borne out by the fact that the uniform and somewhat pleasing bronze-like tint acquired by the weights during the treatment is still to a large extent almost unchanged.

To obtain indubitable evidence as to the intrinsic value of the method described above, the plan was lately tried with other weights but without success. And here we may observe that owing largely to the admixture of one or more sulphur compounds, the quality of the present day coal-gas is very different from that which formerly obtained, and experimental work showed that to this fact must be attributed

Fig. 1.



my non-success with the second set of weights. The difficulty which thus so unexpectedly arose, has now been overcome by a method which for convenience and effectiveness leaves but little to be desired. The new plan is as follows:—

A “vitreosil” crucible having a capacity of 50 c.c. is loosely charged with asbestos fibre to the depth of about half-an-inch, as shown in the figure. A lid *l*, also of vitreosil, is inverted and placed upon the fibre; on this lid are arranged triangular-wise three pointed fragments of porcelain or fused quartz for supporting the weight *w*. The weight having been cleaned and polished and evenly covered with linseed oil, which is applied with the finger and thumb, is stood within the crucible, as indicated in the figure; the

crucible is then covered with its lid, and the whole heated with a Bunsen flame. (It is convenient to adjust the flame so that it extends about half-way up the crucible.) During the heating the weight is frequently viewed, and when it has assumed a golden tint the process is complete; the flame is then removed, and the closed crucible allowed to cool. Finally, the weight is rubbed with an old silk handkerchief and then adjusted. Treated thus, the weight presents the appearance of well-polished and lacquered brass. The protecting film being tough, is not readily defaced, and, if necessary, the polishing may without risk be prolonged: but when the initial operations are correctly performed, nothing beyond a light and brief rubbing is required.

In dealing with a number of weights, great economy both in time and labour may be effected by substituting for the crucible a vitreosil muffle. The muffle is fitted with a rectangular tray, which carries the bits of porcelain, placed in groups of 3, for supporting the various weights. The weights having been arranged, the tray with its charge is introduced into the muffle, which is then closed, suitably heated, and subsequently allowed to cool; the weights are then ready for polishing and adjusting. It may be observed that as the supporting fragments are pointed, they but barely engage the surfaces in contact with them; hence the finished protective film is practically complete.

Some experiments were made to determine the average mass of the protecting film; the results obtained with two weights, the one of 50 and the other of 20 grms., may be cited. The cleaned and polished weights were first accurately weighed, then protected and finished as already described; finally they were re-weighed. The larger weight had increased by  $\cdot 0020$  gm. and the smaller by  $\cdot 0006$  gm. As the respective areas of the two weights were approximately 17 and 12 cm., we find that the average mass of 1 sq. cm. of film was  $\cdot 00012$  gm. in the one case and  $\cdot 00005$  gm. in the other. It was found that the smaller value most nearly represented the weight of a normal film; the other and larger value was exceptional.

Daubeny Laboratory,  
Magdalen College,  
Oxford.



LXXXIII. *Note on the Analysis of Damped Vibrations.*  
By H. S. ROWELL\*.

THE two primary difficulties in the analysis of damped vibrations are the nature of the friction and the position of the zero. In most cases it is sufficient to assume that the friction is a combination of so-called solid friction—a constant, and of fluid friction, proportional to the velocity. In the ordinary view it is inconceivable that these two kinds of friction can coexist at the same time and interface, for the conditions supposed to produce these two kinds of friction are essentially different; dry and wet, or molecular film and measurable film. In practical cases, however, the two kinds of friction can coexist in a system as, for example, where a body slides or turns on dry surfaces and is damped by fluid friction. Thus the equation of motion may be taken as

$$m\ddot{x} + k\dot{x} + c^2x \pm F = 0, \quad \dots \quad (\text{I.})$$

where the signs of  $F$  and of  $\dot{x}$  are the same; put

$$x = X \mp F/c^2,$$

and the solution of equation (I.) is

$$x = \mp F/c^2 - A_0 e^{-\frac{1}{2}kt/m} \cos n't; \quad \dots \quad (\text{II.})$$

where  $n' = \sqrt{n^2 - k^2/4m^2}$

and  $n^2 = c^2/m,$

write  $F/c^2 = S$

and  $k\pi/2mn' = \lambda; \text{ so that } e^{-\lambda} = \delta,$

where  $\delta$  is the logarithmic decrement for half periods.

Assume that a datum line is drawn at a distance  $E$  from the true time axis, and let  $R_i$  be the reading from this datum corresponding to the  $i$ th half swing; then

$$R_0 = E - S - A_0, \quad \dots \quad (1)$$

$$R_1 = E - S + A_0\delta, \quad \dots \quad (2)$$

$$R_2 = E + S - A_0\delta^2, \quad \dots \quad (3)$$

$$R_3 = E - S + A_0\delta^3, \quad \dots \quad (4)$$

$$R_4 = E + S - A_0\delta^4. \quad \dots \quad (5)$$

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Subtracting (1) from (2), and

$$R_1 - R_0 = A_0(1 + \delta). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Subtracting (4) from (2), and

$$R_1 - R_3 = A_0\delta(1 - \delta^2). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Subtracting (3) from (5), and

$$R_4 - R_2 = A_0\delta^2(1 - \delta^2). \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Dividing (8) by (7), and

$$\frac{R_4 - R_2}{R_1 - R_3} = \delta. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Substituting in (6), we have the first amplitude :

$$\begin{aligned} A_0 &= (R_1 - R_0)/1 + \delta \\ &= \frac{(R_1 - R_0)(R_1 - R_3)}{(R_1 - R_2 - R_3 + R_4)} \quad . \quad . \quad . \quad . \quad (10) \end{aligned}$$

Dividing (7) by (6) and adding (2) and (3), we have

$$2E = R_1 + R_2 - \frac{(R_1 - R_3)^2}{(R_1 - R_2 - R_3 + R_4)},$$

which gives the position of true zero.

The solid friction term  $S$  follows from (1), and since  $c^2$  is easily found statically,  $F$  the solid friction of the system per unit mass follows by division.

Where the system is dead-beat, the foregoing method does not apply, and one way of solution is then by tuning of the system by adding mass or increasing  $c^2$  or both so that sufficient equations are determined for elimination.

The curve, of which the vibration in II. is a projection, is an equiangular spiral with alternating origins distant  $2F/c^2$  apart, and it may be traced in either of two ways according to circumstances. In the first place an arithmetic spiral (see *Phil. Mag.*, July 1922, p. 284) may be drawn and the radii vectores shortened logarithmically, or an equiangular spiral may be drawn and portions taken out each subtending  $\pi$ , and such that the initial radius vector of one portion is  $2F/c^2$  less than the final radius vector of the preceding portion. Clearly the parts run smoothly together on account of the equiangular property of the spiral. Here it may be added that since the evolute of the arithmetic spiral is a straight line  $2F/c^2$  long, the curve can be drawn mechanically by coiling a fine thread round two pins  $2F/c^2$  apart. The same curve is described by the hand of the housewife in winding up a card of "mending."

The outstanding difference between solid friction and fluid friction in damped vibrations is that in the one the dissipation per cycle is proportional to the amplitude, whereas in fluid friction the dissipation varies as the square of the amplitude. Since the energy of the motion varies as the amplitude squared, the dissipation per unit time with fluid friction is a constant fraction of the energy of the system, whereas with solid friction the dissipation as a fraction of total energy is inversely as the amplitude. Hence in solid friction the rapid damping of small vibrations until finally the dead region of width  $2F/c^2$  is reached. Clearly in the two systems the envelopes of the two vibration curves may be tangential, in which event solid friction may be mistaken for fluid friction. As the foregoing analysis indicates, five half vibrations or two complete periods suffice not only to safeguard against this possibility, but also to apportion the relative magnitudes of the two sets of frictional forces.

It seems possible that some such analysis as is here outlined may be a useful instrument of investigation in connexion with friction and lubrication, affording at least some sort of criterion in so-called border-line cases.

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LXXXIV. *The Full Effect of the Variable Head in Viscosity Determinations.* By FRANK M. LIDSTONE\*.

SINCE the publication in this Magazine of my paper on the Measurement of Absolute Viscosity (February 1922), it has been pointed out to me by Mr. W. H. Herschel, of the American Bureau of Standards, and by Dr. Guy Barr and Mr. L. F. G. Simmonds, of the National Physical Laboratory, that the logarithmic head correction in the "viscous" term of the equation is, strictly speaking, incomplete, inasmuch as it is based on the assumption that the head varies directly with the velocity. Barr also makes a necessary correction in the final kinetic energy term of the approximate equation, which should read as in equation (2) below.

As no attempt appears to have been made to find a general equation embracing all these corrections, it is here proposed to try to find the exact expression, however laborious and cumbersome, in order to ascertain to what extent the results obtained by means of the ordinary formulæ deviate from the true value. The premises of the whole argument are included in the generally accepted equation,

$$\eta = \frac{\pi r^4 g \rho h}{8 V l} - \frac{V \rho}{8 \pi l t},$$

\* Communicated by the Author.

the coefficient of the K.E. term being taken as unity. This equation is true provided the head  $h$  is constant; but unless some compensating mechanical contrivance is used, such as that adopted by Hyde (Proc. Roy. Soc. A, xevii. 1920), this condition is never absolutely realized in practice, since no matter how the pressure is applied or maintained, as soon as flow starts, there is a change in the hydrostatic head and the total head becomes at once a variable.

We have then, by making  $dt$  depend upon  $dh$ , first to integrate the whole expression with respect to  $h$  over the interval  $H-F$ .

$$\text{Putting } \frac{\pi r^4 g \rho}{8 V l} = A \quad \text{and} \quad \frac{V \rho}{8 \pi l} = B,$$

$$\text{we have} \quad \eta = \frac{A h (H-F) dt}{dh} - \frac{B dh}{(H-F) dt},$$

$$dt = \frac{\eta dh}{2 A h (H-F)} \pm \frac{dh \sqrt{AB} \sqrt{h + \frac{\eta^2}{4AB}}}{A (H-F) h}.$$

The plus sign being obviously the only one permissible, we get, writing  $C$  for  $\frac{\eta^2}{4AB}$ ,

$$\int dt = \frac{\eta}{2 A (H-F)} \int_F^H \frac{dx}{x} + \frac{\sqrt{B}}{\sqrt{A (H-F)}} \int_F^H \frac{\sqrt{x+C}}{x} dx,$$

which, after a little manipulation, gives finally

$$\eta =$$

$$\pi r^4 g \rho t (H-F)$$

$$8 V l \left\{ \log_e \frac{(\sqrt{C+H} - \sqrt{C})(\sqrt{C+F} + \sqrt{C})}{F} + \sqrt{1 + \frac{H}{C}} - \sqrt{1 + \frac{F}{C}} \right\} \quad \dots \dots (1)$$

Now, since  $C$  contains  $\eta$ , to evaluate  $\eta$  from this expression would lead to a number of very unwieldy power series. However, it will be seen that  $C$  must be large in comparison with  $H$  or  $F$ ; hence a small change in  $C$  will not greatly affect the result. As a first approximation, then, we can take  $C$  as equal to

$$\frac{\pi^2 r^4 \eta^2 (H-F)^2}{4 V^2 (\log_e H/F)^2}.$$

Calling this  $C_1$ , we get a value for  $\eta$  which we will call  $\eta_1$ .

We can now get a closer value for  $C$ , namely  $\frac{\eta_1^2 16 l^2}{r^4 g \rho^2}$  or  $C_2$ .

Re-calculating with this value we get  $\eta_2$ , which gives us

$$C_3 = \frac{\eta_2^2 16l^2}{r^4 g \rho^2},$$

from which  $\eta_3$  is calculated, and so on. The first value for  $C$  or  $C_1$  being too large,  $\eta_1$  will be too small. Similarly,  $\eta_2$  will be too large and  $\eta_3$  again too small. Thus  $\eta_1 \eta_2 \eta_3 \dots$  form a series in which the even terms and the odd terms respectively converge asymptotically to the true value for  $\eta$ . The rapid convergence of the series considerably shortens what would otherwise be a rather laborious calculation; three or four terms are sufficient to fix the final value.

As an example, we take one of the standard runnings of water at  $20^\circ \text{C.}$ , and select in particular that one as set forth in detail in Archbutt and Deeley's 'Lubrication and Lubricants,' 3rd edition, p. 157. This example is chosen as there is a considerable fall in the head, although, on the other hand, the kinetic energy term is small. We quote the data of the experiment in full:—

$H = 23.56$	$g = 980.51$
$F = 14.60$	$\rho = 0.99826$
$r = 0.0309$	$V = 4.00756$
$t = 136.0$	$l = 21.991$

From these figures we get as the first value for  $C$  or

$$C_1 = 890.52 \text{ giving } \eta_1 = .0100609,$$

from which  $C_2 = 897.24$  „  $\eta_2 = .0100692$

„  $C_3 = 880.69$  „  $\eta_3 = .0100680$

„  $C_4 = 880.49$  „  $\eta_4 = .0100682,$

from which we can write down the final value of  $\eta$  as .01006818. The value of  $\eta$  calculated from the same data, using the equation

$$\eta = \frac{\pi r^4 g \rho t (H - F)}{8 V l \log_e H/F} - \frac{V \rho (H^3 - F^3) \log_e H/F}{12 \pi l t (H - F)^2 (H + F)}, \dots (2)$$

is .0100721.

The difference between this and the correctly calculated value .01006818 is not very striking, but when one considers that here the kinetic energy term is small (only .5 per cent. of the total) this is not surprising. In order adequately to demonstrate the shortcomings of the ordinary formulæ, it would be necessary to make a running under a considerably increased initial head, in order that the K.E. correction should become appreciable, and to continue the running until the final head was relatively small.



LXXXV. *Quantum Theory of Photographic Exposure.*  
*(Second Paper.)* By L. SILBERSTEIN and A. P. H.  
 TRIVELLI\*.

IN the present paper an account will be given of some additional experimental tests of the light-quantum theory of photographic exposure proposed in the first paper of the same title†, and some further theoretical formulæ will be deduced from the fundamental one given in that paper. First of all, however, due mention must be made of certain very valuable experimental investigations, since published by Svedberg, which seem again to corroborate the theory, also of a paper by Svedberg and Andersson published somewhat earlier, but not brought to our notice until the first paper had been dispatched for publication.

1. Concerning "The Effect of Light," Svedberg and Andersson's paper (Phot. Journal, August 1921, p. 325), dealing under that head with only a very few size-classes of grains (each class, moreover, of a very considerable breadth), contains only the qualitative though definite conclusion that 'for equal exposure the percentage of developable grains is always greater in the class of larger grains.' The quantitative, viz. exponential dependence of this percentage upon the size (area) of the grains, is obtained and well verified experimentally in the case of bombardment by  $\alpha$ -rays. Kinoshita's experiments of 1910 having made it very probable that each silver halide grain hit by an  $\alpha$ -particle is made developable. The latter being granted and the discrete nature of  $\alpha$ -rays being a palpably established fact, the validity of the exponential formula, in our symbols  $k = N(1 - e^{-na})$ , had to follow as a necessary consequence. Its verification is properly a verification of Kinoshita's statement, and by having thus tested it experimentally Svedberg and Andersson have certainly done an important piece of work, especially as Kinoshita's result was contested by St. Meyer and v. Schweidler. In the next section analogous experiments with  $\beta$ -rays are described, but the results thus far obtained are not conclusive apart from enabling the authors to state that one or two  $\beta$ -particles striking a grain do not as a rule make it developable. Finally, returning once more to the effect of light (p. 332),

\* Communication No. 149 from the Research Laboratory of the Eastman Kodak Company. Communicated by the Authors.

† L. Silberstein, Phil. Mag. July 1922, p. 257.

the authors remark only briefly that an analogous conception might also assist in the interpretation of the mode of its action : but add that if the quantum hypothesis be assumed, "the difficulty arises that the real blackening curve has not the exponential form prescribed by this hypothesis if we suppose each halide grain to be made developable when struck by a single light quantum." They seem to forget that the simple exponential formula yielded by a quantum theory relates to the case of equal grains, which is not that of real emulsions, and that in order to obtain the blackening curve (say density  $D$ ) plotted against the logarithm of exposure) that elementary formula has to be integrated over the range of sizes, which presupposes the knowledge of the frequency curve of the emulsion, and the somewhat intricate question of the relation between the photographic "density" and the total of blackened areas has to be treated\*. The latter question, simple though it be for one-layered coatings, becomes particularly intricate in the usual case of many layers of grains. It is for this reason that the best way of testing a similar theory consists in microphotographic counts and planimetric measurements of the individual grains. At any rate, Svedberg and Andersson propose to turn to another more complicated assumption† which, they expect, "will actually predict a blackening curve of S-shape." They propose to discuss this possibility on another occasion.

The second of the papers alluded to, due to Professor Svedberg himself (Phot. Journal, April 1922, p. 186), has a more direct bearing upon our subject, and may turn out to supplement our own tests by offering, as it were, an intermediate link in the conjectured mechanism of the action of impinging quanta or light darts. In this paper Svedberg proposes to explain the behaviour of the grains noted in his preceding paper by a single hypothesis, and to test the latter directly. His hypothesis is that the product of the light action on the halide grain consists of "small centres distributed through the grain or through the light-affected part of the grain according to the laws of chance," and that a grain will become developed if it contains one or more such centres. If  $\nu$  be the average number of centres per grain, the percentage probability that a grain will contain at least one centre (and will therefore be developable) is  $P = 100 (1 - e^{-\nu})$ .

\* Concrete examples of such a kind will be treated in the third paper on our subject.

† Namely, that a certain minimum number of quanta must strike the grain within a certain maximum part of its area in order to "build up a silver nucleus large enough to act as a reduction centre."

Now, it would be enough to assume that these centres are produced by discrete light-quanta impinging upon the grain, and the formula  $P=100(1-e^{-na})$  would follow at once. (For, if  $n$  be the number of light-quanta per unit area, and  $a$  the area of a grain,  $v=na$ .) But Svedberg does not make this assumption\*, and devotes instead the remainder of his paper to testing directly the above formula for the occurrence of at least one centre and the corresponding chance formula for the percentage number of grains having no centres, of those having one or two or three centres, etc., having succeeded in making these centres or, in Svedberg's own words, "the nuclei corresponding to the developable centres," visible and accessible to measurement. For details of these elegant experiments the reader must be referred to the original paper. Here it will be enough to say that the recorded "dots" or visible traces of those centres were found distributed very much in accordance with the probability formulæ, namely, in one experiment with light and one with X-rays. Only two *size*-classes of grains were treated in each of these experiments, and with regard to the dependence upon *exposure* Professor Svedberg (p. 192) has thus far only roughly stated that the percentage number of developable grains "increases approximately exponentially as function of exposure," at least for normal and for over-exposures in the case of light (and probably for all exposures in the case of X-rays) though not for under-exposure to light. The paper is concluded by the remark that to account for the deviation from the exponential formula in the case of low light-exposure, we should probably have to adopt the quantum point of view, and that in the case of light (a quantum of visible light containing 5000 times less energy than an X-ray quantum) "several quanta would have to be absorbed very near one another to form a developable centre." Such a view, however, can easily be shown to be untenable. At any rate, Professor Svedberg proposes to test it by experimental investigations which are planned in this direction.

\* In the discussion which followed upon the reading of Svedberg's paper, Prof. T. M. Lowry mentioned such an assumption of a "bombardment by light corpuscles" as the simplest interpretation of Svedberg's photographs (of the "centres"). Other speakers, however, were rather hostile to such a view, and Mr. B. V. Storr considered it even equally conceivable that the "centres" distributed haphazardly might be present before the light action, but such a state of things would have hardly escaped Svedberg's notice. At any rate, Professor Svedberg will no doubt meet Mr. Storr's objection by appropriate control experiments. Control experiments of such a kind, viz. desensitizing experiments, are now being made by Shepard and Wightman.

The existence of the aforesaid "centres" as seats of incipient development, around which the developer's action gradually spreads, has been known for some years\*, and has been observed, among others, by Trivelli. But the important discovery that these centres are haphazardly distributed is entirely due to Professor Svedberg. If his results are ultimately confirmed by further experiments, especially for a series of different exposures, it will be possible to consider these centres as an intermediate link in the theory proposed in our first paper (the centres marking the spots where the grains were hit by the light-darts). In the meantime, however, our further tests have to be conducted by considering the *last link* of the chain, *i. e.*, by counting the grains of each size-class affected and ultimately developed.

2. Before passing on to the description of our further experimental results, a few words must be said in defence of the property attributed in our first paper to *clumps* (aggregates) of grains which apart from some single grains constituted our chief material. An explanation seems the more necessary, as another recent paper by Svedberg† contains results apparently clashing with what we believe to be the behaviour of clumps with respect to light. The property assumed by us, as the expression of experimental facts, was that a *clump*, *i. e.*, an aggregate of grains in contact with one another, behaves as a photographic unit, by which is meant that if any one of its component grains is made developable, *the whole clump* will be reduced by a sufficiently long development. We have since been able to test this behaviour in a variety of ways.

On the other hand, Svedberg concludes from his experiments that there is no transference of reducibility (developability) from one grain to another "in direct contact" with it. (See especially p. 184, *loc. cit.*)

This apparent discrepancy seems to be due to the circumstance that Professor Svedberg worked with an emulsion (a single kind only) consisting of rather small and almost spherical grains, whereas our material, and especially the so-called W-12-C experimental emulsion, with which all the work in question is being done, consists predominantly of large and very thin, flat polygonal plates or tablets which are in mutual contact either along a whole edge or, still more intimately, are partly piled upon or overlapping each other.

\* Cf. M. B. Hodgson, Journ. Franklin Inst., November 1917.

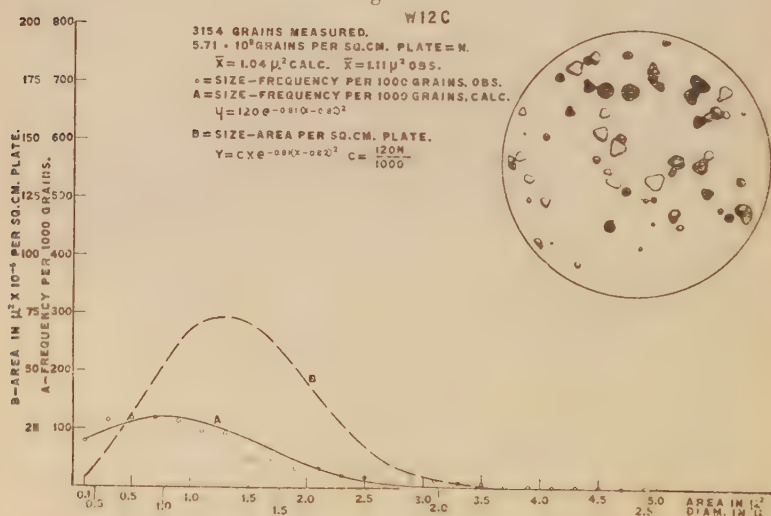
† On "The Reducibility of the Individual Halide Grains," Phot. Journal, 1922, pp. 183-186.



The fine spherical grains of Svedberg could have only at the utmost a point contact, and this might not have been intimate enough. It is even credible that in view of the Brownian motion of these minute bodies there was actually no permanent contact between them, as becomes very likely from Svedberg's remark on page 185, that "even over such a small distance as 1 micron no noticeable transport of silver ions takes place."

At any rate, we have found in our case the property of clumps as units well verified. Without attempting to reproduce in this place all our available evidence\*, we may support and illustrate the said principle by the following data. Fig. 1 represents the frequency curve and, in the

Fig. 1.



inset, a microgram of a sample of grains of the aforesaid W-12-C emulsion. This emulsion was spread over the glass plate in a single layer so as to obtain the maximum number of grains per unit area with the least possible overlapping. The emulsion, after the coating, was kept in its liquid state long enough to enable the majority of the grains to settle with their flat faces on the surface of the glass. Under these circumstances they, and especially the larger grains, form numerous clumps of from 2 up to 33 grains, as will be

\* Discussed in a paper just sent to Phot. Journ. by Trivelli, Righter, and Sheppard. [This paper has since been published in Phot. Journal for September 1922, p. 407.]



manifest from Fig. 2, curve marked *N*. After exposure and development the clumping of the survived grains was determined all over again and is represented by the curve marked *N-K*; the curve marked *K* is the difference of these two curves and represents the clumps affected by light.

Fig. 2.

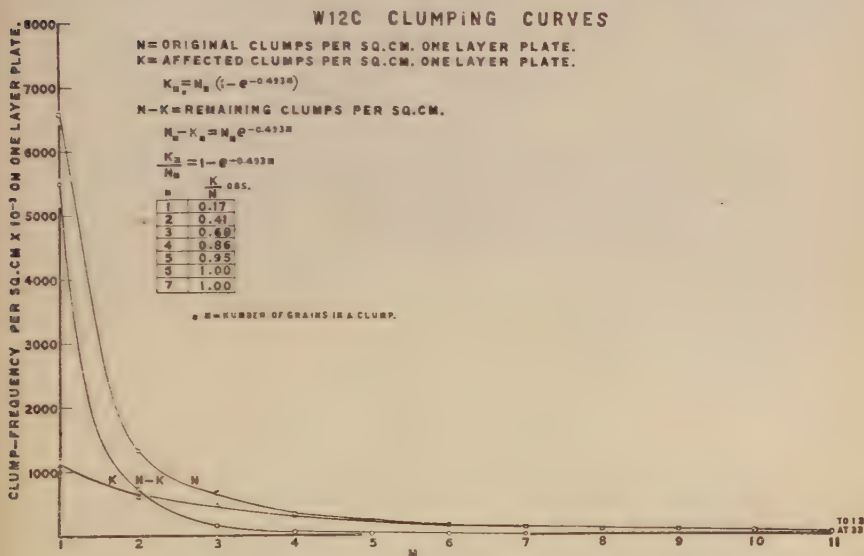
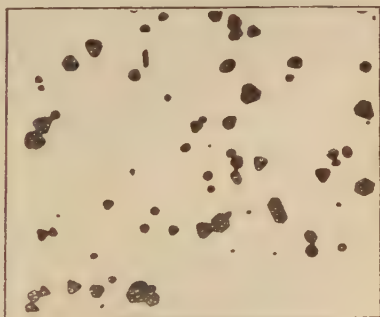
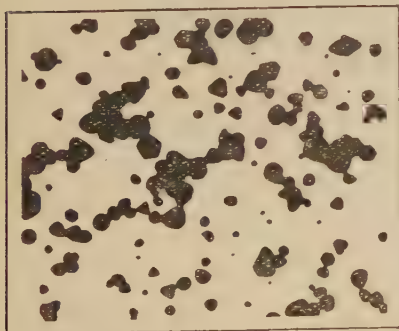


Fig. 3 a.

Fig. 3 b.



This would suffice perhaps by itself to show that our clumps behave as photographic units. But additional evidence is afforded by figs. 3a and 3b, in which all the individuals were carefully blackened by hand on a microgram originally enlarged 10,000 times; the former of these figures refers to the original unexposed one-layer grains, and the latter to

the grains surviving after exposure and development. A glance will show that the majority of clumps, and especially the larger ones, are removed entirely. Of such pairs of samples as figs. 3*a* and 3*b*, about forty were made, and the behaviour was always typically the same. Further and more direct experimental tests of the adopted clump principle are now in progress, notwithstanding that we have but little doubt about its correctness, always, of course, in relation to the material which we are using. And we feel sure that the same principle can be firmly relied upon in what follows.

3. Let us recall that the theoretical values of the percentage number  $y=100k/N$  of clumps affected, as given in the fourth column of the table in our first paper, were calculated by means of formula (12),

$$\log \left( 1 - \frac{k}{N} \right) = -na[1 - \sqrt{\sigma/a}]^2, \dots \quad (12)$$

with the values of the parameters

$$\left. \begin{aligned} n &= 0.572 \text{ per } \mu^2 \\ \sigma &= 0.097 \mu^2, \end{aligned} \right\} \dots \quad (12a)$$

the meaning of all the symbols being as before. The agreement of these values with the observed ones, ranging over 33 classes of grains and clumps, was excellent, thus proving, at any rate, the essential correctness of the formula as far as the dependence on size (area)  $a$  goes.

To test it with regard to the exposure or  $n$ , portions of the same plate were subjected to the action of the same light source, *ceteris paribus*, for one-half, and for one-quarter of the time of the original exposure. The same method of evaluating  $N$  and  $k$  being adopted as before, the results tabulated below under  $y_{\text{obs.}}$  were obtained. Now, without even taking the trouble of retouching the values of the parameters in adaptation to the new observations,  $\sigma$  was taken as in (12*a*) and  $n$  equal to one-half and to one-quarter of its original value, respectively. Since the exposure is, at any rate, proportional to  $n$ , our formula with these  $n$ -values should represent the two new sets of observations. The following table gives in the first row the number of grains in a clump\*, and in the second row the average area  $a$  of each class of clumps, in square microns, as before; the third and

\* Starting from 2, since with these weaker exposures reliable counts of single grains affected could not be secured.

the fifth rows contain the percentage numbers of clumps affected calculated by (12) with  $\sigma=0.097$  and

$$(I.) \quad n = \frac{0.572}{2} = 0.286 \text{ per } \mu^2$$

and (II.)  $n = \frac{0.572}{4} = 0.143,$

respectively, and the fourth and the last rows those observed. The last but one column refers to clumps of 12 and 32 grains, and the fact that almost all of these have been affected ( $y_{\text{obs.}}=100$ ) gives an additional score of verifications of the theory (though in the case of (II.) the observed "100" sets in somewhat too soon).

Grains in Clump		2	3	4	5	6	7	8	9	10	11	...	33
$a \dots\dots$		1.73	3.03	4.88	6.2	7.4	8.6	9.8	11	12	13	...	>25
I. ....	$\left\{ \begin{array}{l} y_{\text{calc.}} \\ y_{\text{obs.}} \end{array} \right.$	28.2	44.2	64.3	74.3	81.0	85.9	89.7	92.4	94.2	95.5	...	99.8
		21	57	63.8	74.5	87.5	96	97	97	96.5	100	...	100
II. ....	$\left\{ \begin{array}{l} y_{\text{calc.}} \\ y_{\text{obs.}} \end{array} \right.$	15.3	25.3	41.2	49.3	56.4	62.6	67.9	73.5	75.9	78.8	...	95.7
		13	37.6	42.3	53	66	82.5	86.5	(?)	89.4	100	...	100

The agreement, although in general not so close as in the previous case, is certainly satisfactory and in three or four instances even remarkably good. Notice especially the case of four-grain clumps which show perfect agreement in all three exposures, the calculated and observed values in the original exposure (*cf.* first paper) having been 87.3 as against 87.1, and now 64.3 and 41.2 as against 63.8 and 42.3. Almost the same is true of the five-grained clumps. But in general the agreement is good enough throughout the array of clumps\*.

4. Notwithstanding the good agreement and the consistency of these three sets of results with regard to the values of  $n$  and  $\sigma$ , some critical remarks must now be made about the meaning of the latter parameter. It will be remembered from the first paper that  $\sigma$  or  $\pi\rho^2$  was originally introduced as the (average) "cross-section" of the light darts, and  $\rho$  as their equivalent semi-diameter, and the mathematical rôle of this finite diameter was fixed by assuming that a grain is made developable only when it is "fully" struck by a light

\* The outstanding discrepancies being attributed mainly to the uncertainty of the (average) sizes  $a$  of the clumps and perhaps also to disregarding the effect of the finite range of  $a$  within each class of clumps. How this finite breadth of the classes can be taken into account will be shown presently.

dart. This gave as the efficient area of a grain, instead of  $a = \pi r^2$ ,

$$a' = a[1 - \rho/r]^2.$$

Now, exactly the same formula would arise if we assumed that, no matter what the thickness of the light darts (and whether it is finite at all), a grain is made developable only when the *axis* of the dart hits it in a point not too near the edge of the target (grain), thus excluding from the total area a boundary zone of a certain breadth  $\rho$ . Such a condition is not altogether fantastic, and one might support it by imagining that if the grain is hit too near its edge, an electron is still ejected and a "centre" of reducibility is produced at the spot, but the wave of development, stopping dead at the edge, has not such a good chance to spread over the whole grain as when the centre is well within the target. If so, then the empirical principle that a grain is either not affected at all or is made developable entirely would require a qualification, viz., the exclusion of that boundary zone. This alternative, therefore, should and can still be tested. If it is supported by experiment, the original interpretation given to  $\rho$  or  $\sigma$  can be abandoned, since it certainly is not very satisfactory. Not that there is anything incredible in the light darts having a finite thickness and a cross section such as one-tenth  $\mu^2$ ; so far as we know, they may be trains of waves of even much larger transversal dimensions. But the unsatisfactory point about this interpretation is that it is hard to imagine why the grain to be affected at all, *i. e.* to have a photo-electron ejected, has to be hit by the whole of that cross section. For, if so, then, unless some light darts have a diameter of the order of  $10^{-8}$  cm., no such things as simple atoms or molecules could ever have their electrons ejected by light\*. Yet, a grain, as a crystal lattice, may, after all, behave as a single molecule, at least in the present connexion, and the original rôle attributed to the cross-section of the light darts, though repugnant, may still turn out to be a useful working hypothesis. To ensure the possibility of being fully hit and therefore affected, even to the smallest available silver halide grains, it would be enough to treat  $\sigma$  in our formula as the average taken over a sufficiently ample interval of sections down to very small ones. It would be premature to enter into quantitative details of the consequences of such an assumption. But it seems proper to mention even at this stage that an assumption

\* Whereas the photo-electric effect has been obtained with gaseous substances, though not beyond every doubt.

of this kind can well be tested experimentally. In fact, if that assumption be correct, then the light traversing two or more equal photographic plates piled upon each other should contain, successively, a larger percentage of the coarser light darts, so that the formulæ of type (12) representing the number of affected grains or clumps of various sizes should have not only a decreasing  $n$ , but also a successively increasing average value  $\sigma$  of the cross-sections of the darts, a comparatively larger proportion of the more slender darts being absorbed each time. In short, we should have a kind of sifting effect. Such experiments which, to be at all convincing, require obviously a much higher degree of accuracy in counts and area measurements, are now in preparation. Their results will be published in a subsequent paper. In the meantime, the parameter  $\sigma$  may and profitably will be retained as a small but desirable correction of the exponential formula without, however, being given either of the alternative interpretations.

It may be well to add here also a few remarks about  $n$ , the chief parameter in the fundamental formula. This was originally defined as the number of light-quanta or darts thrown upon the photographic plate per unit of its area. Now, apart from the generally small correction term containing  $\sigma$ , the parameter  $n$  appears in the formula only through the product

$$p = na,$$

where  $a$  is the area of the grain. Thus, essentially only the value of this product (a pure number) can be determined from microphotographic experiments. Suppose now that the sizes of all grains of the given emulsion were reduced in the same ratio, converting every  $a$  into  $\epsilon a$ ; then, the same experimental value of  $p$  would indicate a number of light darts  $\frac{1}{\epsilon}$  times larger. Now, such would exactly be the position if for every grain not the whole but only a fraction  $\epsilon$  of the area were vulnerable, *i. e.* deprived of an electron on being hit by a light dart. The grain may be sensitive only in spots scattered over its area, and each perhaps of very minute dimensions. Provided that all these spots occupy a fixed fraction  $\epsilon$  of the total area of the grain, the microphotographic counts and measurements could not inform us about the value of this fraction unless the exposure given to the plate is known in absolute energy measure. Thus, for instance, if, as was tacitly assumed,  $\epsilon = 1$ , the number of light darts in the set (I.) of observations just described would lead



to  $n=0.286$  per  $\mu^2$  or about 29 million darts per square centimetre of the plate; but if, say, only one-thousandth of the area of each grain were vulnerable, we should conclude that 29 milliards of darts were thrown upon each  $\text{cm.}^2$  of the plate. But it would be idle to speculate upon this subject and, as far as we can see, the only way of deciding whether that suggestion is correct or not and of determining the value of the fraction  $\epsilon$  is to measure the exposure energy in absolute units \*. Now, in none of our experiments thus far reported was the energy value of the exposure even roughly estimated, not to say measured. But in order to decide this important question, preparations for measurements of this kind are now in progress in this laboratory, and their results will be published in due time.

5. *Effect of finite breadth of size-classes of targets.*—The short name "target" will now be used for either a single grain or a clump of grains in sufficient contact to act as a photographic unit.

In the three sets of observations hitherto reported, the targets were classified according to the number of grains contained in them (from 1 to 33), and for each class the average size (area) was used as  $a$  in the theoretical formula, without taking account of the finite *breadth* of any such class, *i. e.* of the interval,  $a_1$  to  $a_2$  say, over which its individuals ranged. It was not possible with the said classification to secure reliable estimates of this breadth, which, however, for some classes might have been considerable (perhaps of the order  $1\mu^2$ ), and at any rate varied from class to class. It is likely that some of the outstanding discrepancies are due to these neglected factors and especially to the latter.

To eliminate this source of error, and at the same time to avoid the laborious planimetrization of targets within very narrow limits, we propose henceforth to divide the whole material of targets into deliberately broad classes, all of *equal breadth*, say  $2\alpha$ .

If, then, the average size of any of these classes of targets is used as the variable  $a$  in our formula, a correction has to be made for the finite value of  $2\alpha$ . This correction can easily be found.

Disregarding for the moment the  $\sigma$ -term, the number of targets of a class of breadth  $2\alpha=a_2-a_1$  affected by  $n$  darts, is

\* Although even then the final result would be made doubtful by the uncertainty whether the total light energy (as required by Einstein) or only a fraction of it is conveyed in discrete quantum parcels.

by the fundamental formula (7), first paper,

$$k = \int_{a_1}^{a_2} f(a) [1 - e^{-na}] da,$$

where  $f(a)da$  is the number of targets of size  $a$  to  $a+da$  originally present. Now, if  $2\alpha$  is of the order of  $1/2$  or even  $1\mu^2$ , we can take  $f(a) = \text{const.}$  within the integration interval with sufficient accuracy for all of our experimental emulsions. Thus, denoting by  $N$  the original number of targets in the whole class, so that

$$f = f(\bar{a}) = \frac{N}{2\alpha},$$

we shall have 
$$\frac{k}{N} = 1 - \frac{e^{-na_1} - e^{-na_2}}{2n\alpha},$$

or, writing simply  $a$  for the average  $\bar{a} = \frac{1}{2}(a_1 + a_2)$ , and therefore,  $a_2 = a + \alpha$ ,  $a_1 = a - \alpha$ ,

$$\frac{k}{N} = 1 - e^{-na} \cdot \frac{e^{n\alpha} - e^{-n\alpha}}{2n\alpha}$$

Remembering that  $\frac{1}{2}(e^{n\alpha} - e^{-n\alpha}) = \sinh(n\alpha)$ , writing for brevity

$$v = \log \frac{N}{N-k}, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and replacing  $a$  in the chief term by

$$a' = a [1 - \sqrt{\sigma/a}]^{2*},$$

we have ultimately the required formula

$$v = na' - \log \frac{\sinh(n\alpha)}{n\alpha}. \quad . \quad . \quad . \quad . \quad (14)$$

Notice that the correction term depends only on  $n\alpha$ , that is to say, for  $\lambda = \text{const.}$ , on the product of the exposure and the class breadth. If this product is a fraction, such as one-half or even two-thirds †, we can write, up to  $(n\alpha)^4$ ,

$$v = na' - \frac{1}{6}(n\alpha)^2. \quad . \quad . \quad . \quad . \quad (14a)$$

If, as explained, all the contemplated targets of the emulsion are divided into classes of equal breadth  $2\alpha$ , the

\* This is accurate enough provided  $\sigma/a$  is small. In the correction term the semi-breadth  $a$  requires practically no amendment.

† If  $\alpha = 1\mu^2$  and the exposure is as in the previous concrete cases, the value of this product does not exceed 0.6.

correction term in (14) is, for a given exposure, constant throughout the array of classes, and  $v$  plotted against  $a$  should give a straight line. If  $\sigma$  were non-existent or negligible, we should have a straight line for  $v$  plotted against  $a$  itself.

The aforesaid classification of targets and the corresponding formula (14) will be used for analysing all the experiments now in progress. For the present, we are able to quote only one such set of results condensed in the following table.

The targets (grains and clumps alike) were all divided into five classes of equal breadth  $2a=0.60\mu^2$ , ranging from 0.20 to 0.80, from 0.80 to 1.40, etc., as shown in the first column, which gives the average sizes  $a$  in square microns. The third column gives the observed number of targets surviving for every  $N$  targets originally present, each of these data being an average of counts on four different domains of the plate. The fourth column contains the percentage number  $y=100 \frac{k}{N}$  of grains affected, as observed, and the fifth, as calculated by (14), to wit, with

$$n=0.255 \text{ per } \mu^2,$$

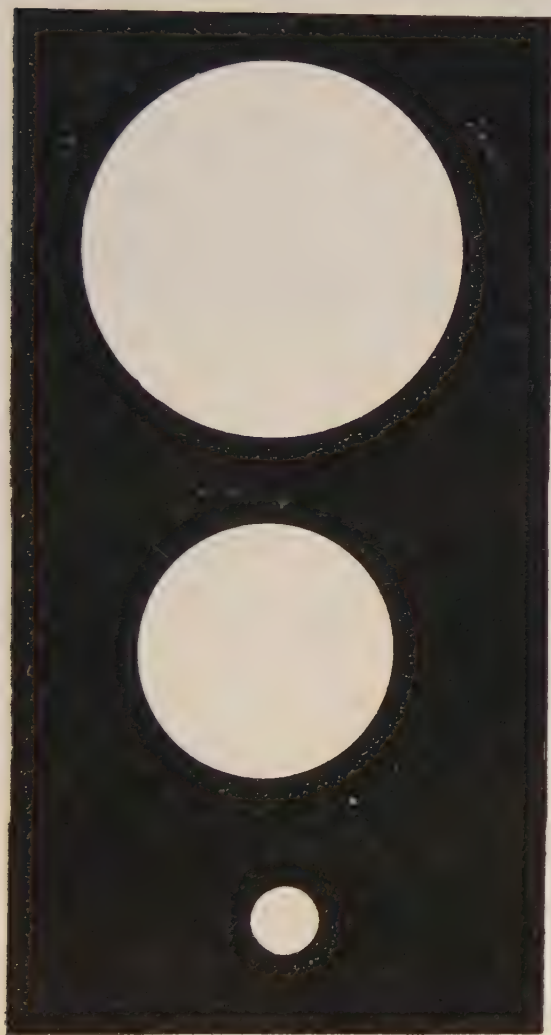
$$\sigma=0.0081\mu^2.$$

$a$ .	$N$ .	$N-k$ .	$y$ obs.	$y$ calc.	$\Delta$ .
0.50	190.3	173.3	8.9	9.0	-0.1
1.10	140.0	103.5	26.0	(20.6)	(+5.4)
1.70	62.6	43.0	31.3	31.1	+0.2
2.30	31.4	18.7	40.4	40.3	+0.1
2.90	19.8	10.3	48.0	48.4	-0.4

The agreement is, apart from the second class, bracketed as an "outlaw," almost perfect. The "cross-section" of the darts, or what  $\sigma$  may stand for, is agreeably about ten times smaller, *i. e.* the diameter three times smaller than that previously obtained with the same light source. This is not to say that the reality and rôle of  $\sigma$  is herewith settled. Yet it is interesting that without  $\sigma$ , that is to say, with  $a'$  in (14) replaced by  $a$  itself, no choice of  $n$  yields such a close agreement. As to the correction term due to the finite class breadth, it may be mentioned that in the present case it amounts (as a subtrahendum from  $v$ ) only to 0.030.

Rochester, N.Y.,  
June 23, 1922.

FIG. 3.



Microphotographs of Orifices 1, 6, and 9.





LXXXVI. *The Discharge of Air through Small Orifices, and the Entrainment of Air by the Issuing Jet.* By J. S. G. THOMAS, D.Sc. (London and Wales), A.R.C.Sc., A.I.C., Senior Physicist, South Metropolitan Gas Company, London\*.

[Plate VI.]

### INTRODUCTION.

THE present paper details some of the results obtained in a preliminary investigation of the conditions determining the entrainment of air by jets of various gases. As there exists considerable uncertainty as to the representation by means of a formula of results for the discharge of gases through fine orifices†, it has been considered desirable to include also a short discussion of results, under this head, obtained during the work.

In the case of the entrainment of air by a jet of gas either lighter or heavier than air, the volume of air entrained per unit volume of gas in the jet is different according as the jet is directed in an upward or downward direction. With a jet of air, such an effect, if present at all, is small. As the great majority of the practical applications of air-entrainment by gas jets issuing from small orifices with which the author is concerned refer to *downwardly* directed jets; it was decided to confine the preliminary experiments with air to such direction.

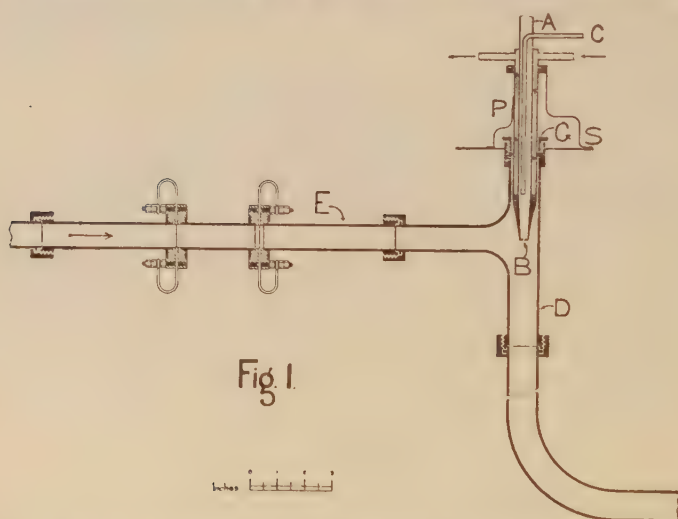
### EXPERIMENTAL.

(a) *The Discharge Tube.*—The flow systems employed in the present investigations are shown in fig. 1. Air was delivered under constant pressure to the brass tube A, the interior surface of which was carefully smoothed, and issued as a jet from the orifice in the disk B, situate at the lower end of the tube. Particulars of the preparation and mounting of the disks and orifices are given later. The tube A was provided with a water jacket through which tempered water flowed, so that throughout the whole series of experiments the temperature of the water in the jacket was maintained constant at 13° C., with a possible variation of 5° C., the temperature being taken by thermometers placed at the inlet

\* Communicated by the Author.

† See, e. g., Buckingham & Edwards, Sci. Papers, Bureau of Standards, vol. xv. pp. 574 *et seq.* (1919–20); Walker, Phil. Mag. vol. xliii. p. 589 (1922).

and outlet to the jacket. The pressure of the air in the tube A at a distance of about 1.5 inches above the orifice was determined by means of the tube C, which was closed at its lower end and provided with a number of small circular openings on its cylindrical surface near its lower end. The tube C was connected with a water manometer, which was read to 1/50 mm. by means of a cathetometer microscope. Calculation showed that the deficit of pressure due to motion of the air in A was negligible. Air delivered from the orifice B passed downwards through the tube D, of vertical length about 10 inches, and bent as shown. The lower end of D was shielded by a large open box, so that disturbances



in the air of the laboratory were very largely prevented from affecting the jet\*. No Venturi tube, to increase the air-entrainment, was inserted in D in the present series of experiments, as it was found that the same tube was not equally suitable for use with all the orifices employed.

(b) *The Air Induction Tube.*—Air set in motion by the action of the jet issuing from the orifice flowed towards the jet through the flow tube E, in which was placed a hot-wire anemometer of the Morris type, constituted of two fine

\* It may be remarked that without such protection, the effect of any atmospheric disturbance upon the indication of the hot-wire anemometer employed is under certain conditions considerably magnified by the operation of the jet. A combination of jet and hot wire, such as described herein, would appear to be an exceedingly sensitive device for indicating small atmospheric movements.

platinum wires. The end of this tube away from the jet opened into a large vessel containing water, which served to saturate the air with water vapour, a condition corresponding to that of the air employed in calibrating the instrument, and to shield the anemometer from outside disturbances. Slightly different calibration curves were employed corresponding to different atmospheric temperatures. The velocity with which the air was set into motion in the tube E by the jet depended upon the length of tube employed. This was chosen of the minimum length consistent with securing steady readings of the anemometer, and was equal to 54 inches.

The jacketted tube A was inserted into the tube D to such a depth that the velocity of air-stream passing over the anemometer wires was a maximum for the pressure employed. A gas-tight joint was then made between the tubes A and D by means of the gland G screwing down on a rubber ring. If for any cause it became necessary to remove the tube A, it could be readjusted to its former position by reading the position of the pointer P with reference to a scale marked on the tube. The pointer S moving over a circular scale served to indicate the azimuthal position of the orifice disk, and was more especially used in connexion with subsequent experiments with multiple-orifice disks.

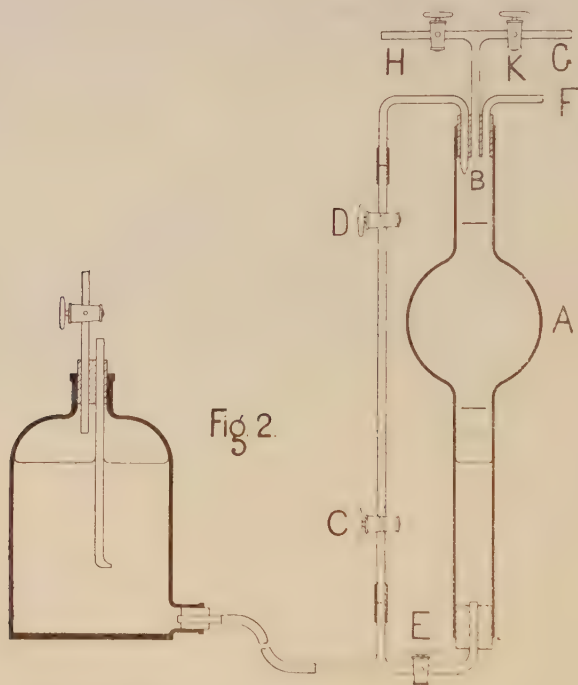
(c) *Measurement of the Discharge.*—The method employed for determining the rate of efflux of air was to determine the time taken for a definite measured volume of air to flow through the orifice. The device employed for this purpose is shown in fig. 2, and is a slight modification of the apparatus employed by Coste\*. The measured volume of air is contained between two marks shown on the vessel A. Water is delivered to the vessel through the jet B from a Mariotte bottle or overflow constant-head device, the rate of flow of water being controlled by means of the cock C. The cock D is fully open during the flow of water through B, and closed while the vessel A is subsequently emptied through the cock E, the cock C being meanwhile unaltered. In this manner the rate of flow of water through B is very conveniently adjusted to the series of increasing rates of flow employed in the present sequence of experiments.

Vessels A of various sizes were employed in the course of the present experiments, the smallest having a volume between marks of 838.2 c.c. and the largest a volume of 7081 c.c. The lower stem of the vessel A extended for a considerable distance below the lower mark, so that the

\* J. Soc. Chem. Ind. vol. xxx. p. 258 (1911).

conditions of flow became steady before the time of the water surface crossing the lower mark was taken. In some of the larger vessels a small bulb was blown on the lower limb for the same purpose.

The pressure in the vessel A was measured by a water manometer connected to F, and the temperature was measured by a thermometer hanging near A. Air was delivered to the orifice through the tube G, and passed over



calcium chloride and then through a small plug of glass wool. Throughout, the volume of air delivered was corrected for pressure, temperature, and humidity. The tube H served for drawing air into A, the cock K being meanwhile closed.

The device maintained a very constant pressure at the orifice, any variation occurring being somewhat less than of the order of 0.5 per cent. of the total pressure.

(d) *Preparation of the Orifices.*—Considerable attention was given to the preparation of the orifices. Throughout,

the endeavour was made to make the orifices as circular and smooth as possible. In the case of the orifices numbered 1-10 in the sequel, these were made in a stiff copper-nickel alloy (88 per cent. Ni, 12 per cent. Cu), 0.0229 cm. thick, and except for the smaller ones were made by means of a machine designed by Dr. Charles Carpenter for the bulk manufacture of single or multiple-orificed injectors for use in gas-burners. By this machine, a disk about 6 mm. in diameter is cut from a sheet of metal, and simultaneously a hole or holes punched in the disk by the passage of a flat-ended accurately cylindrical needle or needles through the disk, which is held meanwhile between blocks, the lower carrying the needle or needles, which after passing through the disk enter accurately bored holes in the upper block. The machine is operated after the manner of an embossing press.

Orifices in disks prepared in this manner possessed a very smooth interior surface, and there was little burr on their outer surfaces. This was readily ground away by rubbing on an oiled stone, and the inner surface finally burnished by means of a cylindrical needle.

The two smaller orifices employed were drilled in the same material, great care being taken to see that they were as accurately circular, and their interior surfaces as smooth as possible.

Fig. 3 (Pl. VI.) shows microphotographs (linear magnification about 37) of representative orifices of the series. They indicate very slight departure from the circular form. Actual measurement showed that the greatest and least radii of any disk agreed to within 1 per cent. except in the case of No. 8, where a maximum difference of about 2 per cent. occurred. A microscopic examination of the interior of the orifices showed that there was present very little roughness in the finished orifices.

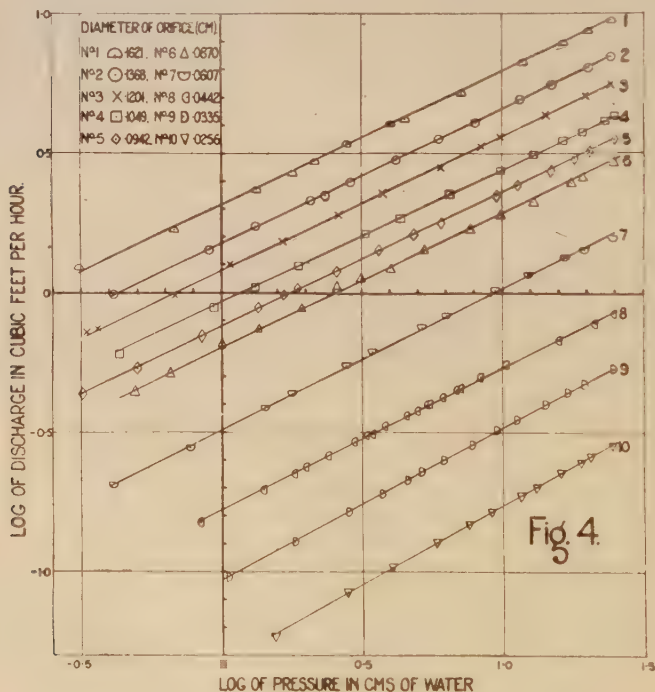
The prepared disk was carefully soldered on to a cap which screwed on to the lower end of the tube B (fig. 1), this cap being then itself soldered on to the tube. It was previously ascertained that all joints in the various parts of the apparatus were gas-tight. Tested under 10 inches of water pressure at various times during the course of the experiments, the leak in the discharge tube when the orificed disk was replaced by a blank of the same thickness, and in the anemometer tube, was found not to exceed 0.001 cubic feet per hour.



## RESULTS AND DISCUSSION.

Table I indicates the general nature of the observations and the calculations based thereon.

(a) *Discharge*.—Fig. 4 shows how the discharge through the various orifices of the series depends upon the pressure and diameter of the orifice. The results shown in this figure all refer to orifices in disks of thickness 0.0229 cm.



Particulars of the diameters of the various disks are given in the diagram and are tabulated in Table II. below. In the figure, the logarithms of the discharge are plotted as ordinate against the logarithms of the corresponding pressures as abscissa, all volumes being reduced to 0° C. and 760 mm. pressure, dry.

It is clearly seen from fig. 4 that the experimental results may be represented algebraically with considerable accuracy by a linear relation between the logarithms of the pressures and discharges respectively. The lines drawn in fig. 4 are the "best fitting" straight lines which can be drawn through

TABLE I.

Orifice No. 5. Thickness of Disk, 0.0229 cm. Diameter of Orifice, 0.0942 cm.

Pressure at orifice. (cms. of water)	Temperature. (0° C.)		Barometer (inches)	Volume between marks on bottle employed. (c.c.)	Time for discharge of measured volume. (secs.)	Corrected discharge through orifice. (c. ft. per hour, dry, measured at 0° C. and 760 mm.)	Anemometer.			Vol. of air entrained by jet. (c. ft. per hour measured at 0° C. and 760 mm.)	Vol. of air entrained by unit vol. of air issuing through orifice.
	Bottle.	Water jacket.					Galvano- meter shunt. (ohms)	Balance resistance. (ohms)	Bridge current. (amp.)		
0.320	12.7	12.5	30.45	2361	661	0.435	10	1014	1.000	72	3.59
0.502	12.5	13.0			542	0.533	10	"	"	110	3.71
0.850	13.0	13.0			411	0.701	10	"	"	258	4.01
1.348	13.3	13.0			325	0.886	10	"	"	394	4.29
1.664	13.5	13.0			295	0.974	10	"	"	466	4.58
1.86	13.5	13.5			275	1.043	6	"	"	314	5.08
2.58	13.5	13.5			239	1.199	6	"	"	379	5.35
3.65	13.5	13.5			201	1.428	6	"	"	468	6.28
4.88	13.5	12.5	30.45		175	1.624	6	"	"	303	6.90
6.08	13.7	12.5			160.2	1.771	2	1028	1.200	335	7.67
9.58		12.5		4116	128.2	2.221	2	1025	"	382	8.31
11.44		12.5			218.8	2.432	2	"	"	400	
15.10		13.0			194.5	2.746	2	"	"		20.64
18.2	14.5	13.0			177.6	3.015	2	"	"		
20.4		13.0			168.2	3.184	2	"	"		
25.0	14.5	13.0	30.44		153.0	3.518	2	"	"		

the several points. Each has been drawn through the "centre of gravity,"  $\frac{\sum x}{n}$ ,  $\frac{\sum y}{n}$  of the respective observations, at an inclination  $\theta$  to the axis of logarithms of pressure given by

$$\tan \theta = m = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sum (x - \bar{x})^2},$$

where

$$\bar{x} = \frac{\sum x}{n} \quad \text{and} \quad \bar{y} = \frac{\sum y}{n},$$

$x$  and  $y$  being the logarithmic coordinates experimentally determined and  $n$  the number of observations.

It follows that the dependence of the discharge  $Q$  (measured at  $0^\circ \text{C.}$  and 760 mm. pressure) upon the excess pressure  $\epsilon$  can, within the limits of pressure employed in the present series of experiments, be represented by a relation of the form

$$Q = A' \epsilon^\alpha \dots \dots \dots \quad (\text{i.})$$

The respective values of  $A'$  and  $\alpha$  are set out later in Table II.

It is of interest here to consider the relation of this equation to that deduced for the relation of discharge to pressure on the assumption that the discharge occurs under adiabatic conditions.

Lamb\* gives for the mass discharge under these conditions the formula

$$q_1 \rho_1 S' = \left( \frac{2}{\gamma - 1} \right)^{1/2} c_0 \rho_0 \left\{ \left( \frac{p_1}{p_0} \right)^{\frac{2}{\gamma}} - \left( \frac{p_1}{p_0} \right)^{\frac{\gamma+1}{\gamma}} \right\}^{1/2} S', \quad (\text{ii.})$$

where  $p_1$  and  $p_0$  are the respective pressures outside and inside the vessel from which the discharge occurs.  $\rho_0$  and  $c_0$  are respectively the density of the gas and the velocity of sound inside the vessel,  $S'$  is the area of the *vena contracta*,  $\gamma$  the ratio of the specific heats, and  $q_1$  the velocity outside the vessel.

Writing  $p_0 = p_1 + \epsilon$ , where  $\epsilon$  is the excess pressure inside the discharge vessel, this expression becomes after some little algebraic reduction, assuming the expansion to take place under adiabatic conditions, and the value of  $\frac{\epsilon}{p_1}$  to be small,

$$q_1 \rho_1 S' = S' \left( \frac{2}{\gamma - 1} \right)^{1/2} c_0 \rho_0 \left[ \left( \frac{\gamma - 1}{\gamma} \frac{\epsilon}{p_1} \right) \left( 1 - \frac{\epsilon}{p_1} \frac{2\gamma + 3}{2\gamma} \right) \right]^{1/2}, \quad (\text{iii.})$$

\* 'Hydrodynamics,' 1906, p. 23.

which may be further transfor ned ; and we obtain, finally,

$$q_1 \rho_1 S' = S' (2\epsilon \rho_1)^{1/2} \left(1 - \frac{1}{2\gamma} \frac{\epsilon}{\rho_1}\right)^{1/2} \quad \dots \quad (\text{iv.})$$

Now it is well known that experimental results are not correctly represented by the assumption of the existence of adiabatic conditions during the discharge of the gas through an orifice in a thin plate\*. The procedure followed by Buckingham and Edwards is to modify the adiabatic relation by the introduction of corrections, taking into account effects due to viscosity, heat conduction, and turbulence, such disturbing effects being regarded as relatively small. We propose to follow a somewhat similar procedure. The adiabatic relation (iv.) failed to represent the experimental results obtained in the present series within the limits of experimental error. The expression  $S' (2\epsilon \rho_1)^{1/2}$  is commonly employed for calculating the approximate mass discharge through orifices in thin plates. The expression  $\left(1 - \frac{1}{2\gamma} \frac{\epsilon}{\rho_1}\right)^{1/2}$ , in which  $\frac{\epsilon}{\rho_1}$  is small, is a small correcting factor. By a suitable slight modification of this factor, a formula may be obtained which represents the present results within the limits of experimental errors.

We take †

$$M = q_1 \rho_1 S' = S' (2\epsilon \rho_1)^{1/2} \left(1 - \frac{\kappa \epsilon}{\rho_1}\right)^{1/2}, \quad \dots \quad (\text{v.})$$

where the value of  $\kappa$  is to be determined from the experimental results. We have from (v.),

$$\frac{d \log_{10} M}{d \log_{10} \epsilon} = \frac{1}{2} - \frac{\kappa \epsilon}{2 \rho_1},$$

assuming  $\frac{\epsilon}{\rho_1}$  to be small and  $S'$  to be independent of the excess pressure. Identifying the left-hand side of this equation with the "best" value of  $\alpha$  in (i.) as determined from the experimental results, we have  $\alpha = \frac{1}{2} - \frac{\kappa \epsilon}{2 \rho_1}$ . The appropriate value of  $\kappa$  is to be determined from a consideration of the "best fitting" value of  $\epsilon$  in this relation. The observations being approximately uniformly spaced through the range of excess pressures employed, and the

\* See, *e. g.*, Buckingham & Edwards, *Sci. Papers*, Bureau of Standards, vol. xv. p. 599 (1919-20).

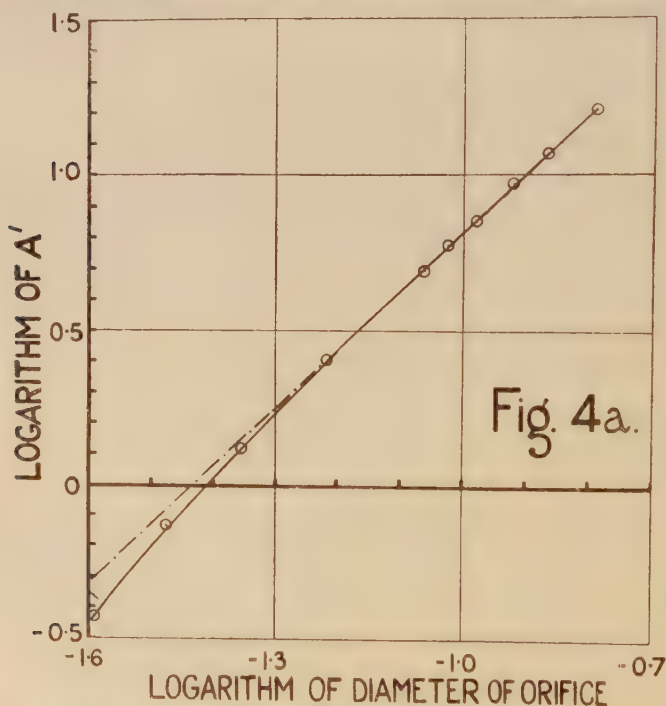
†  $M$  being the mass discharge, is evidently proportional to the volume discharge measured at 0° C. and 760 mm. pressure.

relation between  $\alpha$  and  $\epsilon$  being linear, it follows that the best value of  $\epsilon$  that can be employed in this relation is approximately half the maximum excess pressure. Taking  $\epsilon = 12.5$  cm. of water, we find  $\kappa = 166(0.500 - \alpha)$ .

From (v.), we have the volume discharge  $V_0'$  measured at  $0^\circ \text{C}$ . and 760 mm. pressure given by

$$V_0' = \frac{S'(2\epsilon\rho_1)^{1/2}}{\rho_0'} \left(1 - \frac{\kappa\epsilon}{p}\right)^{1/2},$$

where  $\rho_0'$  is the density of air at  $0^\circ \text{C}$ . and 760 mm.,  $\rho_1$  representing the density under atmospheric conditions during the experiments.  $S'$  was calculated by means of



this formula, employing the value of the discharge corresponding to an excess pressure of 12.5 cm. of water, and the coefficient of contraction of the jet was calculated therefrom. The results are set out in Table II. herewith.

The relation of  $A'$  in the empirical formula  $A'\epsilon^a$  for the discharge given in the fourth column of Table II. to the diameter  $d$  of the orifice is shown in fig. 4a, in which the logarithms of  $A'$  and of  $d$  are plotted as



TABLE II.  
Thickness of Disks, 0.0229.

Disk No.	Diameter, (cm.)	Area S, (sq. cm.)	Empirical Formula for discharge in c.c. per sec. measured at 0° and 760 mm. $A'e^{\alpha}$ .	Corresponding best value of $\kappa$ in $\frac{S'(2\epsilon p)^{\frac{1}{2}}}{\rho_0} \left(1 - \frac{\kappa\epsilon}{p}\right)^{\frac{1}{2}}$ .	Value of $S'$ , (sq. cm.)	Coefficient of Contraction, $\frac{S_0}{S'}$ .
1	0.1621	0.02064	16.16 $e^{0.478}$	3.6	0.01327	0.642
2	0.1368	0.01469	11.79 $e^{0.482}$	3.0	0.00971	0.661
3	0.1201	0.01132	9.36 $e^{0.484}$	2.7	0.00772	0.681
4	0.1049	0.008644	7.12 $e^{0.486}$	2.3	0.00588	0.679
5	0.0942	0.006971	5.94 $e^{0.480}$	3.3	0.00489	0.701
6	0.0870	0.005944	4.93 $e^{0.485}$	2.5	0.00407	0.684
7	0.0607	0.002894	2.54 $e^{0.502}$	0.3	0.00213	0.730
8	0.0442	0.001534	1.32 $e^{0.507}$	1.2	0.001101	0.718
9	0.0335	0.000881	0.736 $e^{0.544}$	7.3	0.000628	0.713
10	0.0256	0.000514	0.369 $e^{0.564}$	10.6	0.000320	0.622

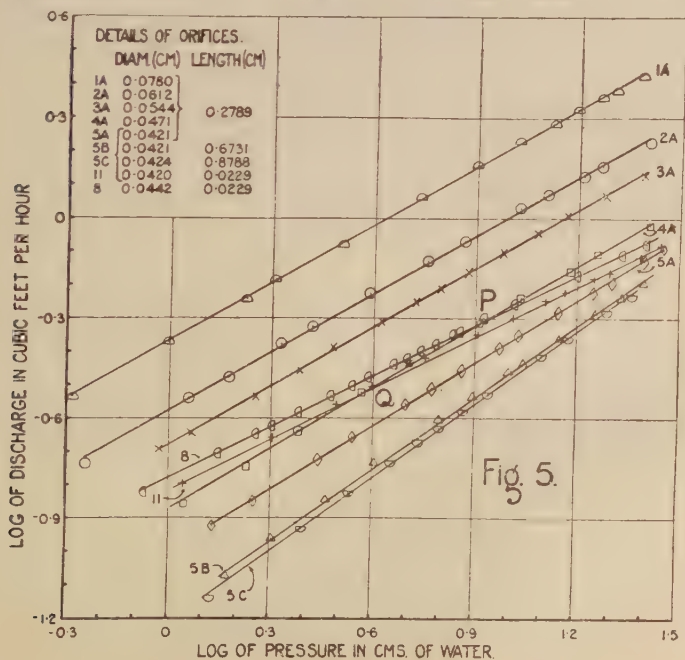
Mean  
2.9

Mean  
0.674



TABLE III.

Channel No.	Length. (cm.)	Diameter of channel. (cm.)	Empirical Formula for discharge ( $A'\epsilon^\infty$ ) (measured in c.c. per sec. at 0° C. and 76 mm.) at excess pressure $\epsilon$ cms. of water.
1 A	0.2789	0.0780	$3.39 \epsilon^{0.579}$
2 A		0.0612	$2.09 \epsilon^{0.580}$
3 A		0.0544	$1.65 \epsilon^{0.585}$
4 A		0.0471	$1.05 \epsilon^{0.611}$
5 A	0.6731	0.0421	$0.783 \epsilon^{0.628}$
5 B		0.0421	$0.509 \epsilon^{0.721}$
5 C		0.0424	$0.479 \epsilon^{0.733}$
11	0.0229	0.0420	$1.19 \epsilon^{0.509}$
8	0.0229	0.0442	$1.32 \epsilon^{0.507}$



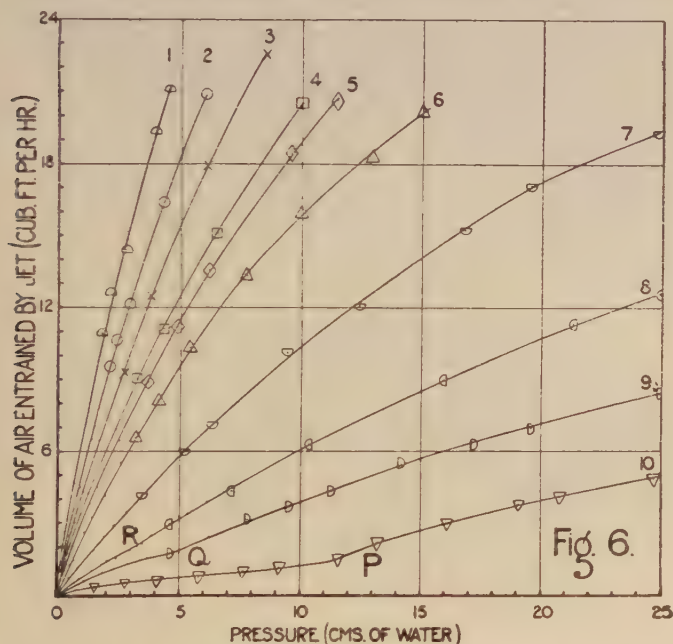
For the channels 1 A-5 A of constant length 0.2789 cm., the value of  $A'$  in the empirical formula for the discharge  $A'\epsilon^{\alpha}$  is given in terms of the diameter  $d$  by the linear relation  $A'=73d-2.33$ . The gradual increase of the index  $\alpha$  in the case of channels 1 A-5 A as the diameter of the channel decreases is seen from fig. 5. It will be noticed that at a pressure a little greater than the maximum employed in the construction of fig. 5, the straight lines shown corresponding to the orifices 11 and 5 A of the same diameter intersect (actually the pressure was found to be 33.2 cm. of water). For pressures greater than this, the discharge through the longer channel is actually greater than that through the shorter channel of the same diameter. A similar phenomenon is represented by the points P and Q, in which the straight lines corresponding to channels 8 and 11 in disks of thickness 0.0229 cut the line corresponding to channel 4a, of slightly larger diameter and of about 12 times the length. The phenomenon is clearly attributable to the difference in the form of the issuing jet in the respective cases of discharge through a channel in a thin or thick plate, the existence of the *vena contracta* in the former case reducing the effective area of the discharge and tending to counterbalance the effect of the greater length of the channel in the latter. Attention has been directed to the existence of a critical length of channel, such that the discharge through an orifice of given size is a maximum, in a recent publication of the Bureau of Standards, Washington\*.

(b) *Air Entrainment*.—In fig. 6, the respective total volumes of air (reduced to 0° C. and 760 mm. pressure, dry) entrained by the issuing jet in the case of each of the jets nos. 1-10, are plotted as ordinates against the respective pressures as abscissæ. The several curves are numbered according to the number of the corresponding orifice. Curves 1-7 represent the normal manner in which the volume of air entrained by a jet of air issuing from a given orifice increases as the pressure at the orifice is increased. As the pressure is increased, an initial approximately linear increase of the total volume entrained is followed by a subsequent increase at a continuously decreasing rate, the curve becoming concave to the axis of pressure. This latter is to be anticipated, as the viscous and frictional drag upon the stream of entrained air increases as the velocity of the stream increases.

The curves corresponding to orifices nos. 8, 9, and 10,

\* Technologic Paper, No. 193, p. 17 (Sept. 6, 1921).

which, as has been shown, must be considered essentially orifices in *thick* disks, exhibit points of inflexion at R, Q, and P respectively corresponding to pressures of 3, 5, and 12 cm. of water. During the course of the experiments with orifices 9 and 10, anomalous behaviour of the jet in the region of these respective pressures was very readily detected, as the galvanometer reading became very unsteady unless the jet was protected very carefully from outside disturbances. Steady deflexions could be obtained by reducing outside atmospheric disturbances to a minimum.

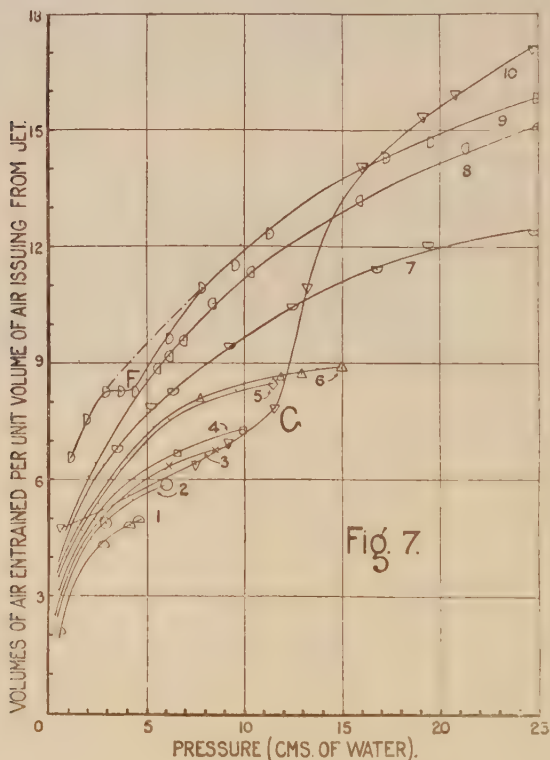


For values of the pressure at the orifice, below the critical value, the galvanometer deflexions were exceedingly steady. The galvanometer deflexion was unsteady until the value of the pressure was increased to a definite value, above the critical value, and thereafter the deflexions were again extremely steady. The phenomenon indicates the existence of a small range of pressures over which the issuing jet is essentially unstable, the efficiency of the jet as regards air entrainment being very considerably affected by slight disturbances in the surrounding atmosphere.

The nature of the instability of the jet is most clearly



seen from a consideration of fig. 7, in which the volumes of air entrained per unit volume of air in the issuing jet are plotted as ordinates against the pressures as abscissæ, in the case of orifices nos. 1-10. Curves 1 to 8 inclusive indicate the normal behaviour of the jet as regards air-entrainment. It is seen that a diminution in the size of the orifice is accompanied in each of these cases by a greater air-entrainment per unit volume of air in the jet. This point is of



importance in the design of gas-burners operating on the Bunsen principle, as it is to be anticipated that a greater degree of primary aeration of the issuing jet of gas can be effected by diminishing the size of the ejector orifice, and employing a multiple-orificed ejector in place of an ejector provided with a single orifice of greater area. In the practical application of this result, however, the several

orifices must be so disposed that the air-entraining power of each individual jet is not reduced by mutual interference of the jets.

It will be clear from the figure that there is a limit of size below which the orifice cannot be reduced without the introduction of disturbing factors adversely affecting the greater degree of air-entrainment normally accompanying reduction of the orifice. This is first seen in the region of F in curve 9, where the degree of air-entrainment is somewhat less than its anticipated value, as shown by the broken line. From curves 9 and 10 it is seen that over the range of pressures up to about 16 cm. of water, the degree of air-entrainment effected by the jet issuing from the small orifice (no. 10) is very much *less* than that effected by the jet issuing from the larger orifice (no. 9).

A similar phenomenon to that described has been observed in the case of coal-gas issuing from a fine orifice. In such a case a flame burning at an orifice under conditions corresponding to those shown at F in fig. 7 would be very sensitive to slight changes of pressure, the degree of air-entrainment varying considerably with a slight increase of pressure. The phenomenon probably explains, at least in part, the existence of *low-pressure* sensitive flames, to which attention has been recently directed, and which were studied in considerable detail by Chichester Bell\*.

With a view to ascertaining the cause of the apparently anomalous behaviour of jets issuing from orifices 9 and 10, similar experiments on air-entrainment were performed with air jets issuing from the comparatively much longer channels nos. 1 A-5 A, 5 B, and 5 C, particulars of which have been given in fig. 5 and Table III. The curves corresponding to those in fig. 6, in which the total volumes of air-entrainment were plotted as ordinate against the pressures as abscissa showed well-marked points of inflexion in the cases of channels 3 A, 4 A, 5 A, 5 B, and 5 C, these points corresponding to pressures respectively equal to 2.5, 5.0, 7.5, 11.0, and 13 cm. of water.

The curves for channels nos. 1 A-5 A showing the degree of air-entrainment per unit volume of air in the jet are shown in fig. 8. The curves generally resemble those given in fig. 7. One distinction is of importance. A comparison of curves 3 A and 4 A with curves 9 and 10 in fig. 7 indicates

\* See, e. g., 'Nature,' vol. cviii. p. 532 (1921). Phil. Trans. Part 2, pp. 383-422 (1886).

that the effect referred to is not so pronounced in the case of jets issuing from the longer channels. The same is seen from curves 4 A and 5 A in fig. 8.

The existence of turbulence in the jet naturally suggests itself as the cause of the phenomenon referred to. It is clear that as the effect occurs only over a limited range of pressures, and is not present at the higher pressures employed in the present series of experiments, and as moreover the mean

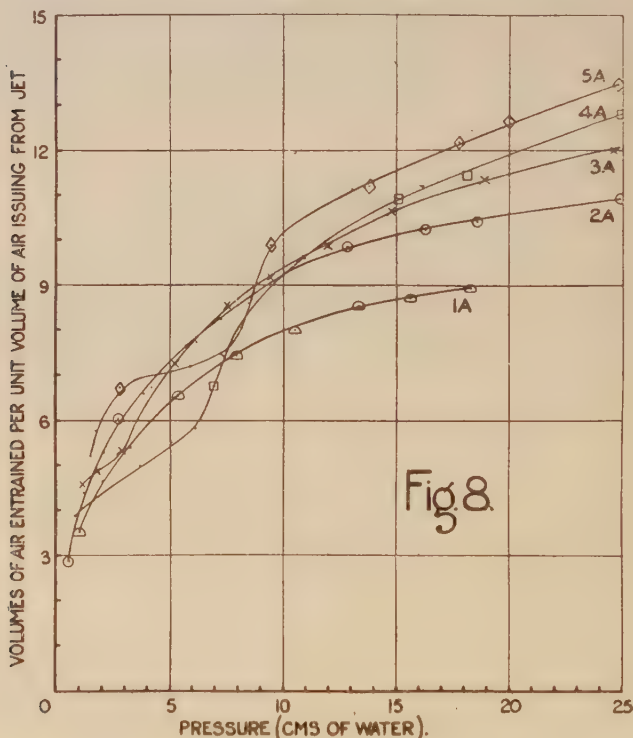
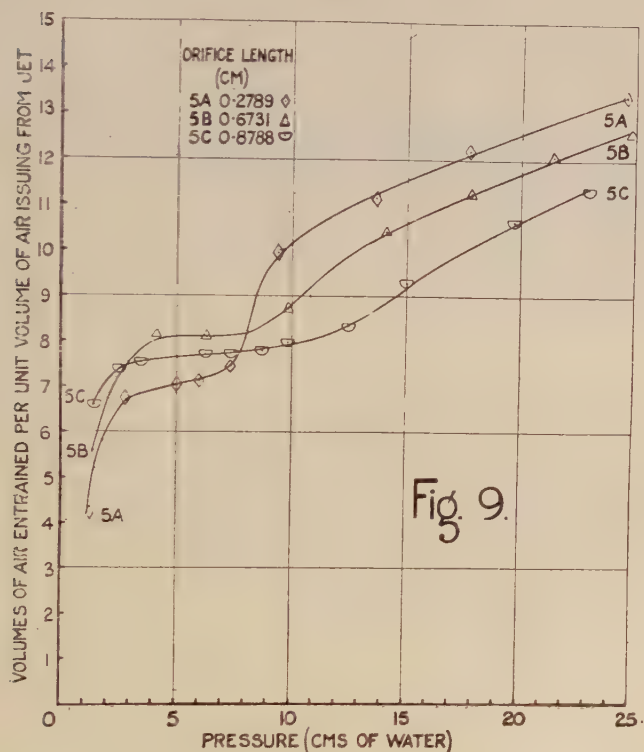


Fig 8.

velocity in the jet for this range of pressures is considerably below the critical velocity at which turbulent flow occurs, the turbulence referred to is impressed upon the jet on entering the orifice. It is therefore to be anticipated that the effect would be less pronounced in the case of long channels than in the case of small channels, as in the former case the unstable turbulence initially impressed upon the stream would die away to a greater extent than in the latter case. This, as has just been stated, was found to be

the case and is clearly brought out in fig. 9, which gives the results obtained with channels all of the same diameter but of different lengths. The effect is much less marked in the case of the longer channel 5 C than in the case of the shorter channel 5 B or 5 A.

The absence of the effect at the lower pressures is attributable to motion of the gas at such low pressures being



in general so slow that little initial unstable turbulence is impressed upon the stream, and any such turbulence, if produced, is damped out before emergence of the jet from the orifice. At the higher range pressures at which the effect is absent, the passage of the air into the channel approximates to stream-line motion, the air within the reservoir immediately adjacent to the disk being practically stagnant, so that little turbulence is produced by a sudden

change of direction of motion of the air entering the channel or orifice.

The work detailed above was carried out in the Physical Laboratory of the South Metropolitan Gas Company; and the author desires to express his sincere thanks to Dr. Charles Carpenter, C.B.E., for the provision of facilities for carrying out the investigations, and for his continued interest in the work.

709 Old Kent Road, S.E. 15.

14 Aug., 1922.

LXXXVII. *The Chemical Constants of some Diatomic Gases.*  
By J. R. PARTINGTON, D.Sc.\*

1. **T**HE Theorem of Nernst supplements the two Laws of Classical Thermodynamics by assigning to the constant of integration,  $I$ , of the Reaction Isochore of Van't Hoff (1) a value otherwise determinable only by experiment with the particular system of materials under consideration:

$$d \log_e K / dT = Q_v / RT^2 \quad . \quad . \quad . \quad (1)$$

$$\log_e K = -Q_v / RT + I. \quad . \quad . \quad . \quad (2)$$

$$\text{According to Nernst, } I = \sum ni, \quad . \quad . \quad . \quad (3)$$

*i. e.* the integration constant is represented as the algebraic sum of the products of the numbers of interacting molecules ( $n$ ) by the *chemical constants* ( $i$ ) of the various *pure* gaseous materials taking part in the reaction.

2. The value of  $i$  is the constant of integration of the Clapeyron-Clausius equation, simplified by the usual approximations

$$\lambda_T = RT^2 \cdot d \log_e p / dT, \quad . \quad . \quad . \quad (4)$$

where  $\lambda_T$  is the latent heat of vaporization per gram molecule at the temperature  $T$ . The value of  $\lambda_T$  as a function of temperature is given by Kirchhoff's equation

$$\lambda_T = \lambda_0 + \int (C_p - c) dT, \quad . \quad . \quad . \quad (5)$$

where  $C_p$  is the molecular heat of the vapour at constant pressure, and  $c$  that of the condensed phase. Thence

$$\log_e p = -\frac{\lambda_0}{RT} + \frac{1}{R} \left( \int_0^T \frac{dT}{T^2} \right) (C_p - c) dT + i. \quad . \quad (6)$$

\* Communicated by the Author.



According to Langen \*, the value of  $C_p$  may be split into a translational term independent of  $T$  and equal to  $5/2 \cdot R$  for a diatomic gas, and a rotational term,  $C_{pr}$ , dependent on  $T$ . Equation (6) is then written

$$\log_e p = -\frac{\lambda_0}{RT} + \frac{5}{2} \log_e T + \frac{1}{R} \int_0^T \frac{dT}{T^2} \int_0^T (C_{pr} - c) dT + i, \quad (6a)$$

$$\log p (\text{atm.}) = -\frac{\lambda_0}{RT} + 2.5 \log T + \frac{1}{4.571} \int_0^T \frac{dT}{T^2} \int_0^T (C_{pr} - c) dT + C. \quad (6b)$$

The constants  $i$ ,  $C$  then supply the terms to (3), and permit the integration of (1). The values of  $C$  have been calculated from a consideration of the experimental data by Langen for several gases. Values of  $C$  had been calculated by Nerust † by a somewhat arbitrary method, and although his results provide a satisfactory approximation for particular problems, they are not in accordance with modern theories of specific heats, as was pointed out by the author in 1913 ‡.

3. It will be noted that the equations so far given do not provide a complete solution of the problem of predicting, from purely thermal magnitudes (heats of formation and specific heats) and universal constants, the behaviour of materials when placed together under specified conditions in the absence of passive resistances §. The final step was taken in the case of *monatomic* substances by Sackur and by Tetrode ||, who were able to calculate the value of  $i$  in terms of universal constants. If the temperature is reduced to such an extent that the atomic heat of the condensed phase becomes negligible in comparison with unity, then (6) becomes

$$\log_e p = -\frac{\lambda_0}{RT} + 2.5 \log_e T + i, \quad . \quad . \quad . \quad (6c)$$

since  $C_{pr}$  is zero for a monatomic substance, and the value

\* A. Langen, *Z. Elektrochem.* xxv. p. 25 (1919).

† 'Recent Applications of Thermodynamics to Chemistry,' 1907. *Theoretische Chemie*, 8-10 Aufl., 1921, p. 799.

‡ 'Thermodynamics,' 1913, p. 496.

§ It may be that the influence of passive resistances could be included by introducing a "heat of activation," in the sense understood by Perrin, Trautz, W. C. M. Lewis, and others, in connexion with  $\lambda$ , but this problem is not considered in the present communication.

|| Sackur, *Ann. d. Physik*, xl. p. 67 (1913). Tetrode, *ibid.* xxxviii. p. 434, xxxix. p. 255 (1912). Stern, *Z. Elektrochem.* xxv. p. 66 (1919).

of  $i$  is then given, according to these authors, by

$$i = \log_e \frac{(2\pi m)^{3/2} k^{5/2}}{h^3}, \quad \dots \quad (7)$$

where  $m$  is the mass of the atom,  $k$  is Boltzmann's constant ( $R/N_0$ , where  $N_0$  is Avogadro's constant), and  $h$  is Planck's constant. With numerical values (see § 7 below), and  $p$  in atm., this gives

$$C = -1.589 + 1.5 \log M, \quad \dots \quad (7a)$$

where  $M$  is the atomic weight, referred to the same standards as  $N_0$ .

4. The object of the present communication is the extension of this line of investigation to a *hypothetical* diatomic molecule which, it is believed, represents with some approximation the structure of a particular group of gases\*. A general solution would obviously enable us to predict the results of all types of gaseous reactions without recourse to experiment, and would provide a long-sought solution to a fundamental problem of chemical affinity.

The method of calculation adopted is that of generalized statistical mechanics†. An isolated system, possessing an energy  $\epsilon$ , and composed of a large number of molecules which exert no forces on one another, is assumed to be definable in terms of a set of generalized coordinates  $q_1, q_2, \dots$ , and a corresponding set of generalized momenta  $p_1, p_2, \dots$  related by the first canonical equation of Hamilton,

$$\dot{q}_1 = \partial \epsilon / \partial p_1. \quad \dots \quad (8)$$

According to the Quantum Theory,

$$H = \iint \dots dq_1 dq_2 \dots dp_1 dp_2 \dots,$$

which is independent of time and of the particular choice of coordinates, has a definite value for each element of the generalized space (*Elementargebiet*). In the case of an ideal gas, the mean energy  $\bar{\epsilon}$  coincides with the energy  $\epsilon$  in any point of the element, and

$$\Sigma e^{-\frac{\epsilon_n}{kT}} = \iint \dots \frac{dq_1 dq_2 \dots dp_1 dp_2 \dots}{H} e^{-\frac{\epsilon}{kT}}. \quad \dots \quad (9)$$

\* Partington, Trans. Faraday Soc. 1922.

† J. W. Gibbs, 'Elementary Principles of Statistical Mechanics,' Planck, *Wärmestrahlung*, 4 Aufl. 1921. Jeans, 'Dynamical Theory of Gases.'

5. In the first case we suppose the gas molecule to consist of two identical atoms rigidly attached to each other at a fixed distance. In addition to the coordinates of the centre of gravity we require two angles,  $\theta$  and  $\phi$ , defining the direction of the molecular axis. Rotation about this axis is, as usual, ignored. We then have

$$q_1=x; q_2=y; q_3=z; q_4=\theta; q_5=\phi;$$

$$p_1=m\dot{x}; p_2=m\dot{y}; p_3=m\dot{z}; p_4=mK^2\dot{\theta}; p_5=mK^2\sin^2\theta\dot{\phi},$$

where  $K$  is the radius of gyration.

The energy of this molecule is given by

$$\epsilon = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \frac{mK^2}{2}(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2) + \epsilon_0, \quad (10)$$

where  $\epsilon_0$  is the energy of the molecule at rest in the generalized space. Thus

$$\Sigma e^{-\frac{\epsilon_n}{kT}} = \frac{m^3 K^3}{H} \iiint \dots \sin^2\theta dx dy dz d\dot{x} d\dot{y} d\dot{z} d\theta d\phi d\dot{\theta} d\dot{\phi} e^{-\frac{\epsilon}{kT}}. \quad (11)$$

The limits of the multiple integral are the boundaries of the element of volume for  $x, y$ , and  $z$ ; the angles 0 and  $2\pi$  for  $\theta$ ; the angles 0 and  $\pi/2$  for  $\phi$ , and all the velocities from  $-\infty$  to  $+\infty$ . Hence, if  $V$  is the total volume,

$$\Sigma e^{-\frac{\epsilon_n}{kT}} = \frac{2\pi V K^3}{H} (2\pi m k T)^{5/2} e^{-\frac{\epsilon_0}{kT}}.$$

The free energy,  $\psi$ , of the system is then given by\*

$$\psi = -kTN \left\{ \log_e \Sigma e^{-\frac{\epsilon_n}{kT}} - \log_e \frac{N}{e} \right\}, \quad (12)$$

where  $N$  is the total number of molecules in the volume  $V$ , say  $N=N_0$ , the number of molecules in one gram-molecule. In the above case

$$\psi = -kTN_0 \log_e \frac{2\pi V K^3 e}{H N_0} (2\pi m k T)^{5/2} + N_0 \epsilon_0. \quad (13)$$

For equilibrium between the vapour and the condensed phase

$$\psi' - \psi = p(V - V'), \quad (14)$$

in which dashed symbols refer to the condensate. Substituting in (14) from (13), and neglecting small terms, we find

$$k \log_e \frac{2\pi K^3 V e}{N_0 H} (2\pi k m T)^{5/2} - \frac{\epsilon_0 - \psi'/N_0}{T} = k.$$

\* Planck, *loc. cit.* p. 210.

But  $\epsilon_0 - \psi'/N_0 = \lambda_0'$ , the latent heat of vaporization per molecule at  $T=0$ ; hence, with the substitutions  $pV = N_0 kT = RT$ ;  $N_0 m = M$ ; and  $\lambda_0 = N_0 \lambda_0'$ , we find

$$\log_e p = -\frac{\lambda_0}{RT} + \frac{7}{2} \log_e T + \frac{5}{2} \log_e M + \log_e \frac{K^2 (2\pi k)^{7/2}}{(h N_0^{1/2})^5}, \quad (15)$$

where  $H = h^5$  in the generalized space of five dimensions\*.

6. For a diatomic gas of the type considered in § 5,  $C_p = 7/2$ , and hence

$$\log p(\text{atm.}) = -\frac{\lambda_0}{4 \cdot 571 T} + C_p \log T + 2 \cdot 5 \log M + 2 \log K + 12 \cdot 730. \quad (15a)$$

( $k = 1 \cdot 37 \times 10^{-16}$ ;  $h = 6 \cdot 55 \times 10^{-27}$ ;  $N_0 = 6 \cdot 06 \times 10^{23}$ ; 1 atm. = 1013250 abs. units. See Millikan, *Phil. Mag.* July 1917).

The equation representing the vapour-pressure of a diatomic substance at such low temperatures that the energy of the condensate is negligible in comparison with that of the vapour (which will generally occur before the gas begins to lose its diatomic character, except in the case of molecules of very small mass and diameter, such as hydrogen) is

$$\log_e p = -\frac{\lambda_0}{RT} + C_p \log_e T + i,$$

$$\text{or} \quad \log p(\text{atm.}) = -\frac{\lambda_0}{4 \cdot 571 T} + C_p \log T + C.$$

By comparison of (15) with these we find

$$\left. \begin{aligned} i &= 2 \cdot 5 \log_e M + 2 \log_e K + \log_e \frac{(2\pi k)^{7/2}}{(h N_0^{1/2})^5}, \\ \text{or} \quad C &= 2 \cdot 5 \log M + 2 \log K + 12 \cdot 730. \end{aligned} \right\} \quad (16)$$

7. In the case considered,  $K^2 = r^2$ , where  $r$  is the radius of the molecule. For oxygen,  $r = 1 \cdot 8 \times 10^{-8}$  cm.,†,  $M = 32$ , hence  $C_{O_2} = 1 \cdot 001$ . The four values given by Langen (*loc. cit.*) range from 0.539 to 1.021, the mean being 0.829. In the case of nitrogen,  $r = 1 \cdot 9 \times 10^{-8}$  cm.,  $M = 28$ , hence  $C_{N_2} = 0 \cdot 904$ . Langen gives only one value for nitrogen,  $-0 \cdot 05$ , from which one can perhaps only conclude that it is somewhat less than the value for oxygen. The case of

\* The various methods of quantizing rotations are kept in mind.

† Jeans, 'Dynamical Theory of Gases,' 2nd edit. p. 341; all values of  $r$  from this.

hydrogen is probably not satisfactorily covered by formula (16), since the value of  $C_p$  becomes appreciably reduced within a region of temperature before the value of  $c$  for the condensate becomes negligibly small. Hydrogen, therefore, should behave in a manner intermediate between that of a diatomic gas (equation 16) and that of a monatomic gas (equation 7). Nernst\* has applied (7) to hydrogen, and after the application of small corrections, has found  $C_{H_2} = -1.23$ ; whereas Langen, by formula (6), finds  $-3.767$ . Equation (16) gives  $C_{H_2} = -2.255$  ( $M = 2.016$ ;  $r = 1.34 \times 10^{-8}$  cm.).

8. In the case of gas molecules composed of two different atoms rigidly bound together, the calculation is similar, except that the angle  $\phi$  is now, since the molecule is no longer symmetrical, to be taken between the limits 0 and  $\pi$ . In the cases to be considered it is still a sufficient approximation to take  $K^2 = r^2$ . This case is, therefore, covered by the addition of  $\log 2$  to (16). In the case of carbon monoxide,  $r = 1.90 \times 10^{-8}$ ,  $M = 28$ ; hence  $C_{CO} = 1.205$ , whilst Langen gives  $-0.04$ . For nitric oxide,  $r = 1.86 \times 10^{-8}$ ,  $M = 30$ ; hence  $C_{NO} = 1.263$ , whilst Langen finds  $0.92$ . Perhaps all that can be definitely said of Langen's values for these gases is that they are somewhat larger than the value for nitrogen, and it is noteworthy that Nernst's empirical values for the compound gases are larger than those for the elementary gases:  $3.5$  for CO and  $3.5$  for NO, as compared with  $2.8$  for  $O_2$  and  $2.6$  for  $N_2$ †.

It is believed that the above method of calculation gives results which are in all cases of the right order, and that the values deduced by other methods are still so divergent that a more searching comparison is not at present possible. It is hoped that the method will shortly be extended to gases with more complex molecules, in which internal motions also occur. If these are considered as small vibrations, their energy can be represented as the sum of squared terms in the coordinates, and the above method can be applied to them without difficulty.

East London College,  
University of London.

† *Grundlagen des Neuen Wärmesatzes*, 1918, p. 150. There are a few misprints in this section, e. g. in (120)  $-0.5T$  should be  $-0.5\ln T$ , and  $(2\pi m)^{1/2}$  should be  $(2\pi m)^{3/2}$ .

\* *Theoretische Chemie*, p. 799 (1921).



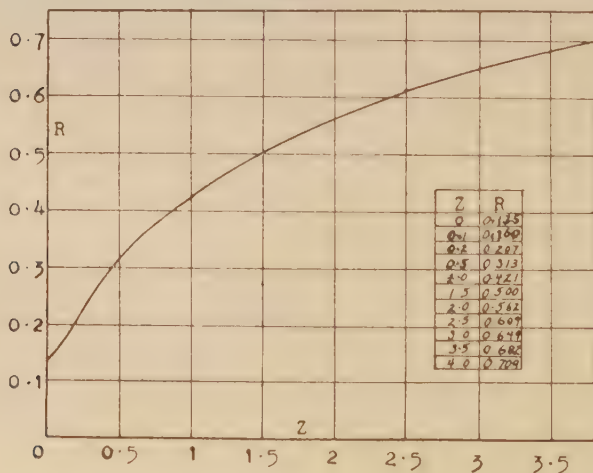
LXXXVIII. *The Motion of Electrons in Carbon Dioxide.*  
By M. F. SKINKER, *Rhodes Scholar, Exeter College, Oxford* \*.

IN some recent publications of the Philosophical Magazine, Prof. J. S. Townsend and Mr. V. A. Bailey † describe their experiments on the motion of electrons in hydrogen, nitrogen, oxygen, and argon.

In this paper I wish to give the results of similar experiments with carbon dioxide and to compare the results.

The apparatus used had the same dimensions and was similar to the one described in the above papers. The electrode  $E_2$ , in fig. 1 ‡, however, was not exactly under the slit in B, but was 0.6 millimetre to the right. In order to find the velocity of agitation  $u$  it is necessary to find the normal distribution-curve when the centre of the stream is 0.6 millimetre from the centre of the electrode  $E_2$ . In this case R, the ratio of the current received by the central electrode to the total current, is given by the curve in fig. 2, Z being the electric force in volts per centimetre.

Fig. 2.



The curve differs slightly from the curve which corresponds to the case in which the centre of the stream coincides with the centre of the electrode  $E_2$ .

\* Communicated by Prof. J. S. Townsend, F.R.S.

† Phil. Mag. vol. xlii. Dec. 1921, and vol. xliii. March 1922.

‡ Fig. 1, vol. xlii. p. 875.

The calculation of this curve will be explained in a future paper by Prof. J. S. Townsend and Mr. V. A. Bailey.

In order to find the velocity of the electrons in the direction of the electric force, two different magnetic forces may be used. With this eccentricity of 0.6 millimetre the stream may be deflected 1.9 millimetres to the left or 3.1 millimetres to the right. In these experiments all deflexions were to the right, as the determinations with the larger deflexions are the more accurate.

The results of the experiment are given in Table I., where

$p$  is the pressure in millimetres of mercury,

$k$  the factor by which the kinetic energy of the electron exceeds the kinetic energy of a molecule of a gas at 15° C.,

$W$  the velocity of the electrons in the direction of the electric force in centimetres per second.

TABLE I.

$p$ .	$Z$ .	$Z/p$ .	$k$ .	$W \times 10^{-5}$ .
20.23	4.16	0.206	1.19	—
9.82	2.08	0.222	1.283	1.18
9.82	4.16	0.444	1.29	2.41
5.06	2.08	0.411	1.277	2.45
9.82	8.33	0.888	—	4.91
5.061	4.16	0.822	1.36	4.55
2.49	2.08	0.835	1.36	4.67
5.06	8.33	1.647	—	9.42
2.49	4.16	1.67	1.72	9.81
1.26	2.08	1.66	1.64	9.47
5.06	16.67	3.30	—	22.4
2.49	8.33	3.32	2.88	23.8
1.26	4.16	3.29	2.79	23.6
.62	2.08	3.32	2.89	24.5
2.49	16.67	6.64	22.1	82.4
1.26	8.33	6.59	21.1	82.4
.63	4.16	6.64	23.1	81.4
2.49	33.33	13.4	60.6	118
1.26	16.67	13.2	60.1	124
1.26	33.33	26.4	81.3	142
.63	16.67	26.6	91	150
.63	33.33	53.2	147	202

The values of  $W$  and  $k$  are plotted against  $\frac{Z}{p}$  in figs. 3-6, together with the curves for hydrogen and nitrogen.

Fig. 3.

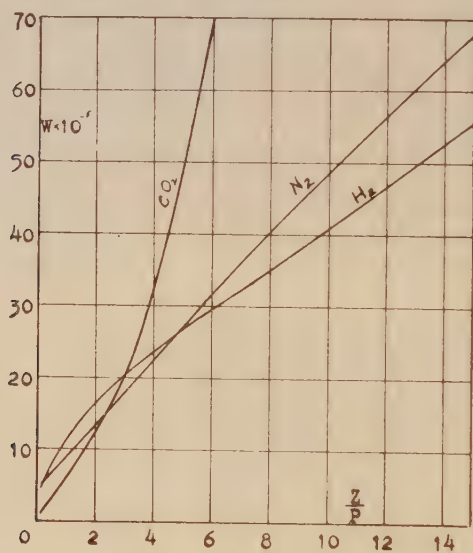


Fig. 4.

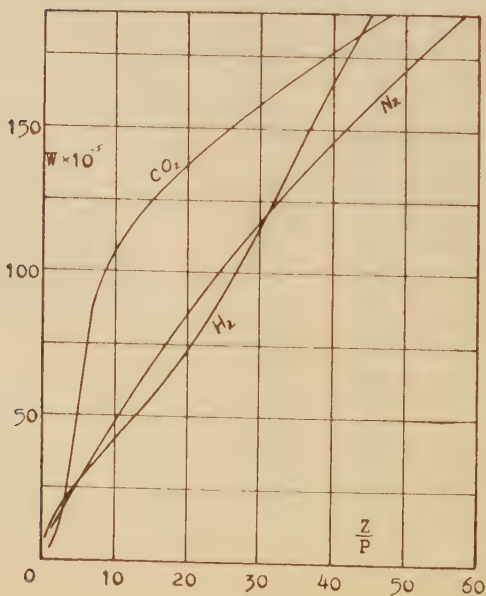


Fig. 5.

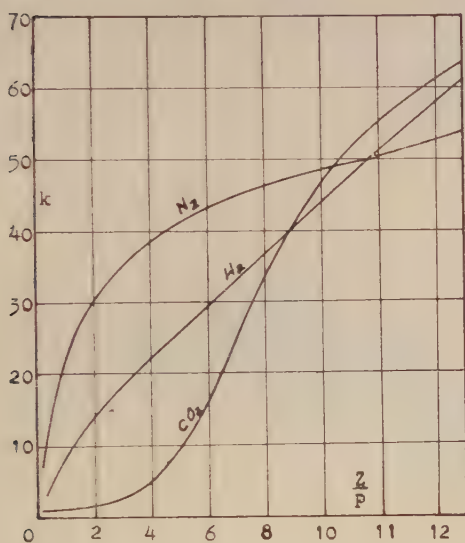
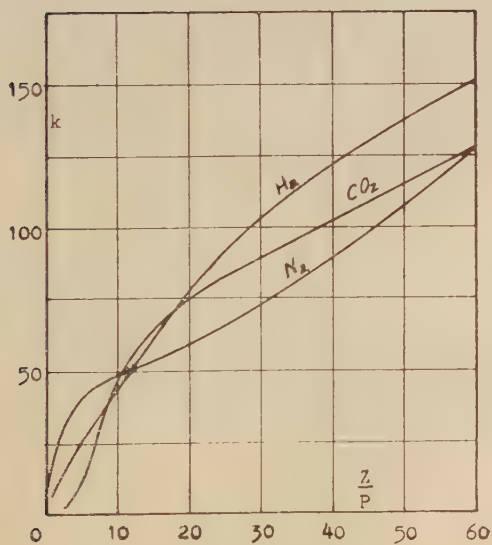


Fig. 6.



In the following table,  $u$  is the velocity of agitation of electrons in centimetres per second,  $l$  the mean free path of the electron in centimetres,  $p$  the pressure of the gas in millimetres of mercury, and  $\lambda$  the proportion of energy of the electron lost in collision with a molecule.

The formulæ connecting  $u$ ,  $l$ , and  $\lambda$  with the quantities  $k$  and  $W$  being :—

$$u = 1.15 \times 10^4 \times \sqrt{k},$$

$$W = \frac{Z}{p} \times \frac{e}{m} \times \frac{lp}{u} \times 0.815,$$

$$\lambda = 2.46 \times \frac{W^2}{u^2}.$$

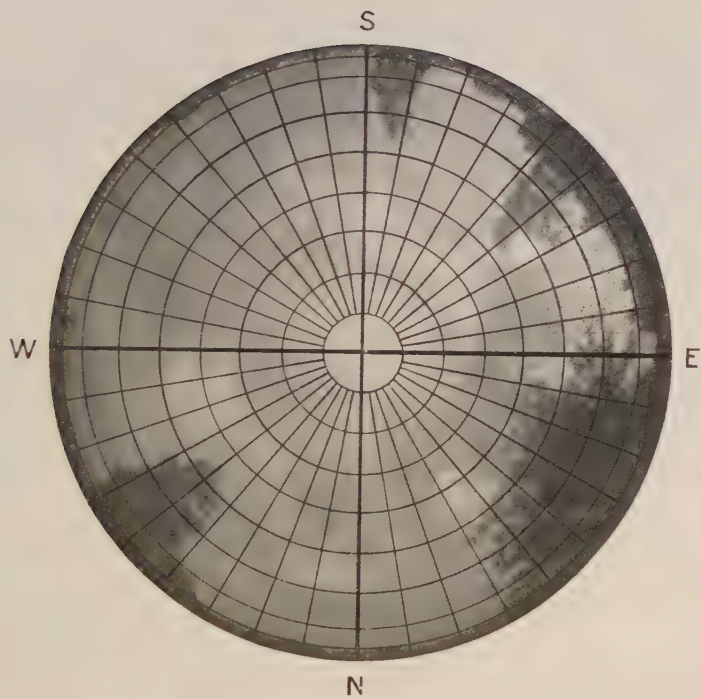
TABLE II.

$Z/p$ .	$k$ .	$W \times 10^{-6}$ .	$u \times 10^{-6}$ .	$lp \times 100$ .	$\lambda \times 10^4$ .
50	139	19.5	135.7	3.67	506
40	117.5	17.75	124.8	3.84	497
30	96	15.9	112.8	4.15	487
20	75	13.8	99.5	4.76	472
10	47	10.8	78.9	5.91	460
6.5	20.7	7.8	52.4	4.36	543
5.0	9	5.0	34.5	2.39	516
4	4.8	3.2	25.2	1.40	397
3	2.3	2.0	17.5	.809	321
2	1.8	1.18	15.4	.630	144
1	1.5	.55	14.1	.538	37.4
0.5	1.3	.25	13.1	.454	8.95
0.25	1.2	.12	12.6	.419	2.34

In order to determine whether or not there were any ions in the stream, the magnetic force was increased, to see if the stream were completely deflected off  $E_1$  and  $E_2^*$ . This was found to be possible when using a magnetic force which was comparatively small and which would not have been sufficient to deflect ions from the plates. Also the quantity  $k$  and the velocity  $W$  were found to remain constant with different values of  $Z$  and  $p$  when  $\frac{Z}{p}$  was constant; these results show that there could not have been any permanent ions formed in the gas.

\* Fig. 1, vol. xlii. p. 875.







With values of  $\frac{Z}{p}$  greater than 30 the loss of energy in a collision is comparatively large, so that the velocity of agitation is less than seven times  $W$ , and in these cases the formula for  $W$  in terms of  $l$  and  $u$  is not so accurate as in the cases where  $\frac{Z}{p}$  is less than 30 and  $u$  comparatively large.

Table II. shows for the higher values of  $\frac{Z}{p}$  that the mean free path increases with decrease of  $u$ , but for the lower values it decreases with decrease of velocity of agitation. In the other gases the mean free path increases for the smaller values of the velocity of agitation.

The values of  $\lambda$  show that with this gas there is a remarkable increase in the loss of energy of an electron in a collision for comparatively small increases in the velocity of agitation from the values  $13 \times 10^7$  centimetres to  $15 \times 10^7$  centimetres per second.

Electrical Laboratory, Oxford,  
July 1922.

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LXXXIX. *A Wide Angle Lens for Cloud Recording.* By  
W. N. BOND, M.Sc. (Lond.), A.R.C.S., A.Inst.P., Lecturer  
in Physics, University College, Reading\*.

[Plate VII.]

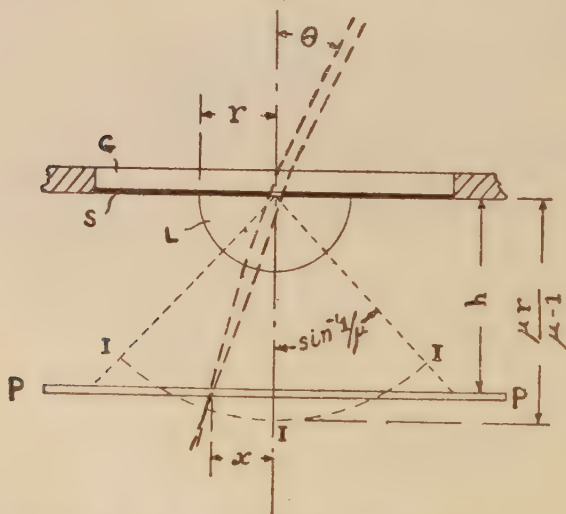
THIS paper consists of a short description of a lens that might be used for obtaining a photographic record of the clouds visible at a meteorological station at definite times, or for similar purposes, such as recording lightning flashes.

The special feature of the lens is that its field of view embraces a complete hemisphere; so that if the lens be arranged to face vertically upwards, all the clouds visible at the station at any one time can be recorded photographically on a single flat plate or film. The resultant photograph (see Pl. VII.) is circular, any clouds at the zenith being reproduced in the centre of the circle, and any near the horizon appearing near the edge of the circle. Such apparatus might, of course, be used at two stations simultaneously to obtain the altitudes of the clouds.

\* Communicated by the Author.

The lens in its original form consists of a glass hemisphere  $L$  (fig. 1) of radius  $r$ . The light is incident on the plane face, which is covered by a thin screen  $S$ , except for a small circular aperture at the centre. It will be seen that a ray incident in the plane of the outer face of the lens will be refracted at the critical angle. Furthermore, all refracted rays will arrive almost normally at the hemispherical face of the lens, and will subsequently converge to form an image, which, for objects at infinity, will lie on part of a sphere  $III$ , concentric with the hemispherical face of the lens and of radius  $r\mu/(\mu-1)$ , where  $\mu$  is the refractive index of the lens. The emergent cone of rays will in practice have a total angle of slightly less than  $90^\circ$ ; and if

Fig. 1.



the aperture in the screen  $S$  is small enough, the whole image will be sufficiently in focus on a flat plate  $PP$  placed at a distance from the plane face of the lens equal to the mean distance of the various portions of the true image  $III$  from this plane face.

The screen  $S$  should be covered on the outer side by a plane plate of glass  $G$ , the whole being cemented together. This arrangement avoids the finite thickness of the screen  $S$ , preventing some or all of the light incident at fairly oblique angles from entering the lens.

It will be seen that the photographic plate should be placed at a distance  $h$  from the plane face of the lens of about  $2.5r$  (*i.e.* rather less than  $r\mu/(\mu-1)$ ). It is easy

to show that a cloud at an angle  $\theta$  from the zenith will appear on the plate PP at a distance  $x$  from the centre of the image, given by

$$x = h \sin \theta / \sqrt{\mu^2 - \sin^2 \theta}.$$

The lens is, of course, not corrected for chromatic aberration, but this might be largely removed by employing a monochromatic filter, which could be closed so as to facilitate the photographing of clouds.

The finite size of the image of a distant point source, due to the plate PP not coinciding with the true image III, can be shown to be very approximately  $d/7$ , where  $d$  is the diameter of the aperture in the screen S. If the hole in the screen be of diameter  $d = r/20$ , the aperture of the lens is roughly f. 50; and the finite size of the image mentioned above results in a blurring at the zones which are most out of focus, which is equivalent to an uncertainty in  $\theta$  of about  $\frac{1}{4}^\circ$ .

The illumination of PP becomes less for large values of  $\theta$ , but the effect does not seem sufficiently pronounced to be objectionable in cloud photography, and need not be considered in detail.

The angle of the field of view of the lens could be increased yet further by replacing the outer plane plate G by a plano-convex lens, having its curved face outwards. This arrangement might be used if it were desired that the photograph should show the horizon and slightly below it. An advantage of this arrangement would be that the zone for which the image is most cramped together would not be at between  $80^\circ$  and  $90^\circ$  from the zenith, but say from  $95^\circ$  to  $105^\circ$ , thus enabling the record of clouds near the horizon to approach more nearly the clearness of that of clouds at the zenith than would be the case if a simple hemispherical lens were used.

It may be mentioned that the lens gives views similar to those seen by a fish in water. The apparatus has, however, probably been reduced to the simplest form advisable, though a less perfect image could be obtained by placing the photographic plate in contact with one side of a thick parallel plate of glass, the other side being covered by a thin screen pierced by a small hole.

Finally, it will be seen that when using the simple hemispherical lens, or the thick plate of glass just described, only two constants (viz.  $h$  and  $\mu$ ) need be known accurately, to enable a complete network of degrees to be constructed for use in interpreting the photographs.



XC. *A Problem in Viscosity: The thickness of liquid films formed on solid surfaces under dynamic conditions.*  
 By The Research Staff of the General Electric Company  
 Ltd., London. (Work conducted by F. S. GOUCHER and  
 H. WARD.) \*

[Plate VIII.]

*Summary.*

THE problem of determining the thickness of the liquid layer coating a solid body drawn out of a liquid is discussed theoretically and practically. It is shown that if the solid is a flat slab of infinite width, the forces determining the thickness are those of gravity ( $g$ ) and viscosity ( $\eta$ ), and that the relation between thickness ( $t$ ), density ( $\rho$ ), and velocity of drawing  $v_0$  is  $t^2 = \frac{2v_0\eta}{\rho g}$ .

If the solid is a fine wire of radius  $r$ , surface tension is dominant and gravity negligible. If  $\gamma$  is the surface tension, the relation must be of the form  $\frac{t}{r} = f\left(\frac{\eta v}{\gamma}\right)$ . It is found empirically that  $f\left(\frac{\eta v}{\gamma}\right)$  is of the form  $4.8 \frac{\eta v}{\gamma}$  in c.g.s. units.

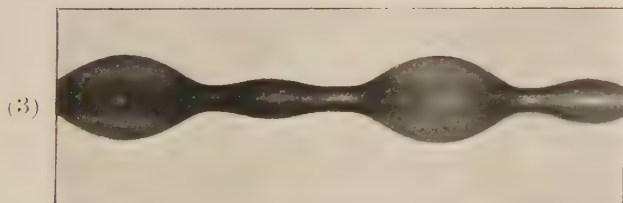
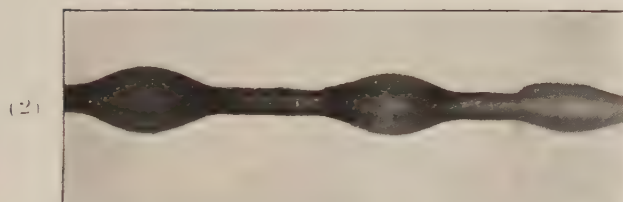
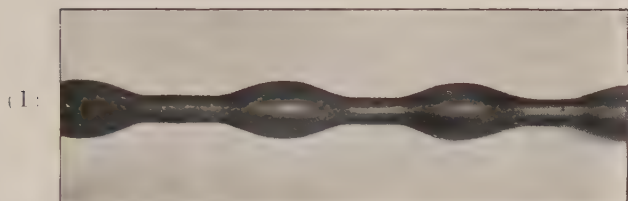
These results apply to suspensions if (1) the diameter of the suspended particles is not greater than  $t$ , (2) the effect of the particles in increasing  $\eta$  is taken into account.

There is no evidence of any special cohesion between solids and liquids wetted by them other than that which prevents slipping at the interface.

In many important industrial processes solid surfaces are coated with a layer of liquid by drawing them out of a bath of the liquid. The enamelling of wires or tubes is such a process, and so in all essentials is painting with a brush. We are aware of no theory or even complete experimental investigation directed to determine how the thickness of the liquid layer produced in such circumstances varies with the properties of the liquid, the solid surface, the velocity of drawing, and other possible factors. The experiments described in this paper show that the matter is surprisingly simple.

\* Communicated by the Director.

FIG. 5.



$\times 100$

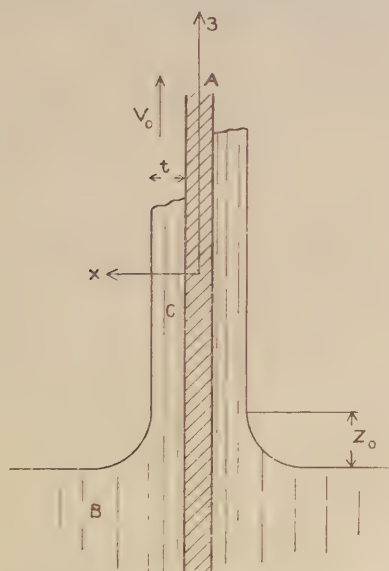


*I. Theory.*

The factors which must be effective appear at once from fig. 1, which shows a longitudinal section of the solid A drawn vertically with velocity  $v_0$  out of the liquid B. Observation shows at once that at least in some circumstances, the thickness of the liquid layer C is constant for a distance above B very much greater than  $t$ .

Consequently it is reasonable to assume that in C the stream lines are vertical: and if they are vertical, continuity requires that the velocity  $v$  along any one stream line is constant. This constant velocity must represent a balance

Fig. 1.



between the forces acting on any element of the layer, and of these forces one must be that due to viscosity of the liquid and another that due to gravity. If the solid is a plain slab of infinite breadth perpendicular to the diagram, it is difficult to see what other force can act; it is possible that, if it is sufficiently small, some special force of cohesion between liquid and solid is effective, but we shall see that the facts can be explained adequately without introducing such a force. If, on the other hand, A is a cylinder, surface tension may be effective; for, owing to the curvature of the

outer surface of C, this tension will produce an increase of pressure in C which will not be balanced by any corresponding pressure over the ends of the layer. Accordingly, the liquid in the layer will be squeezed out of it at the lower end, and, possibly, at the upper.

The balance of these forces must be such that the outer layer of C is at rest relatively to the liquid B in order that the continuity of the liquid surface may be preserved.

This last condition may appear puzzling; for if the solid is continually moving upwards carrying the liquid C with it, it would seem that the outer layer of this liquid must be moving upwards. What really happens is that the inner layer, next to the solid, moves upward with the velocity of the solid; the other layers move upwards with a velocity continually decreasing outwards, the difference between the velocities of different layers providing viscous forces necessary to counteract gravity or surface tension. If the layer at distance  $x$  from the solid moves upward with velocity  $v$ , it will require a time  $l/v$  after the drawing starts before a layer of thickness  $x$  is found at a height  $l$  above the liquid. Strictly speaking, it will require an infinite time before the layer of full thickness, corresponding to  $x=0$ , appears at a finite height above the surface. But a consideration of the numerical values in the equation about to be deduced will show that the time required for a layer of thickness differing inappreciably from  $x$  to form at a distance of several centimetres above the surface amounts only to a few seconds. Accordingly, if we wait a few seconds between starting the drawing and taking observations the thickness of the liquid on the surface will be practically equal to that corresponding to  $v=0$ .

With these considerations in mind the complete solution of the case of the infinite slab is easy.

If  $x$  be taken horizontal and  $z$  vertical, with the origin on the surface of the slab; and if  $\rho$  is the density,  $\eta$  the viscosity of the liquid,  $v$  its velocity relative to B, we have

$$\frac{d}{dx} \left( \eta \frac{dv}{dx} \right) = \rho g, \quad \dots \dots \dots (1)$$

with the boundary condition that at  $x = t \tau \frac{dr}{dx} = 0$ .

$$\text{Hence} \quad v = \frac{\rho g}{\eta} \left( \frac{x^2}{2} - t x \right) + v_0; \quad \dots \dots \dots (2)$$

at  $x=0$  if there is no slip  $v=v_0$ , the velocity with which the



slab is drawn upwards:  $t$  must adjust itself so that this condition is fulfilled, *i. e.*

$$t' = \sqrt{\frac{2v_0\eta}{\rho g}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is not easy to measure  $t$  accurately while the slab is moving, and of course, if it is stopped, the conditions are changed at once. In practice the liquid layer usually sets, owing to cooling, evaporation, etc., at some little distance about the liquid surface. In our experiments we have used a liquid with a melting-point above room temperature, so that it freezes on the slab a little distance above the surface of the bath; we can then measure the thickness  $t'$  of the solid film. If in these conditions the assumptions we have made so far are legitimate, we have from the equation of continuity

$$t'v_0 = \int_0^t v dv \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which gives 
$$t' = \frac{1}{3}t = \sqrt{\frac{2v_0\eta}{9\rho g}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

But the assumptions cannot be accurately true, for since the thickness of the layer decreases as the liquid cools and as its viscosity increases, the stream lines cannot be vertical or of constant velocity. We shall consider the effect of this failure of the assumption in III.

If the surface were a circular cylinder of radius  $r_0$  we should have instead of (1)

$$\frac{d}{dr} \left( \eta r \frac{dv}{dr} \right) = \rho g \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which, using the same assumptions as before, gives in place of (2)

$$v = v_0 + \frac{1}{2} \frac{\rho g}{\eta} \left\{ \frac{r^2 - r_0^2}{2} - (t + r_0)^2 \log \frac{r}{r_0} \right\} \quad . \quad . \quad (7)$$

When  $\frac{t}{r_0}$  is small (7) gives

$$v_0 = \frac{1}{2} \frac{\rho g}{\eta} t^2 \text{ as in (3).}$$

If  $\frac{t}{r_0}$  is not small we may expect surface tension forces to be appreciable. The calculation is then more difficult and we can give no complete solution. The flow would appear to depend on the exact form of the meniscus at the surface of the liquid. But a dimensional argument gives us some information.

If both gravitational and surface tension forces are appreciable, we must have

$$f\left(\frac{t}{r_0}, \frac{r_0}{r_s}, \frac{\eta v}{\gamma}, \frac{\eta v}{\rho g r_0^2}\right) = C, \quad . \quad . \quad . \quad (8)$$

where  $r_s$  are lengths and  $C$  a no-dimensional magnitude characteristic of the system. We shall see later that conditions can be found in which the gravitational forces are inappreciable compared with those due to surface tension. If we assume that this condition is fulfilled and assume further that there is only one independent length  $r_s$ , viz.  $r_0$ , then (8) reduces to

$$\frac{l}{r_0} = f\left(\frac{\eta v}{\gamma}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

It should be pointed out, however, that the last assumption is precarious. For when surface tension is effective,  $z_0$  the height of the meniscus over which the pressure due to surface tension varies from  $\gamma(r_0 + t)$  to zero is likely to be as important as  $r_0$ . (8) can be valid over the whole range only if  $z_0$  is proportional to  $r_0$ . But if it is true, we should expect the importance of the surface tension relative to the gravitational terms to be measured by  $\frac{\gamma}{\rho g r_0^2}$ , so that the gravitational terms may be neglected when this expression is large.

The dimensional argument cannot, of course, prove that the distribution of the liquid as an even layer is stable. The analogy of a water jet strongly suggests that it will not be stable. If it is not stable, the conditions may be entirely altered by freezing the layer as soon as it is formed. This possibility will be considered later; but if they are not greatly altered, the effect of freezing will merely be, as before, to introduce a constant factor. The form of (9) will not be changed.

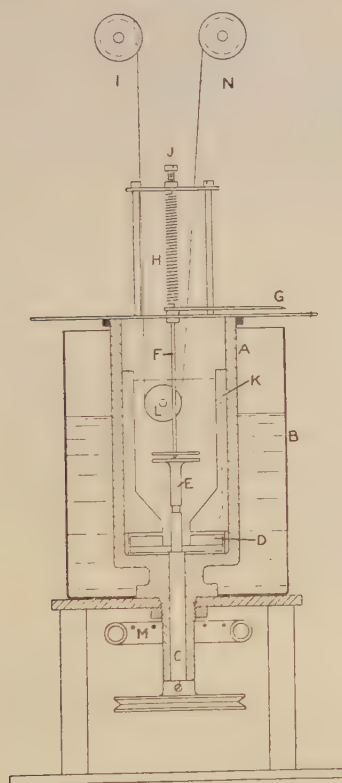
Another case of some interest may be mentioned briefly, although we have not investigated it experimentally. If a cylindrical tube is drawn out of the liquid, the gravitational and surface tension forces will act in the same direction in the layer on the outside of the tube and will act in opposite directions in the layer on the inside. If the dimensions of the tube are such that the two sets of forces are comparable, the layer will therefore be thicker on the inside. It is interesting to speculate what will happen inside the tube when the surface tension forces are great compared with the gravitational. It is easy to see that in such conditions the

liquid must fill the entire cross-section of the tube, and will not begin to fall out of the tube till the column becomes so high that the gravitational forces become appreciable and the conditions supposed are violated.

## II. Apparatus.

In order to test these theoretical considerations arrangements were made to draw metal strips or wires at known speeds out of a stable liquid, the viscosity of which could be

Fig. 2.



varied by change of temperature and which would solidify at ordinary temperatures, so that the thickness of the layer could be measured.

The apparatus was designed so that the viscosity of liquid and the surface tension could be measured under the conditions prevailing when the wire or plate was drawn from it.

The essential features were the viscosimeter, the surface tension apparatus, and the drawing device.

(a) *Viscosimeter*.—The viscosity was measured directly by means of the torsional force exerted on a flat disk by another disk parallel and near to it when both are immersed in the liquid and when the second disk is made to rotate at a fixed speed. If the geometrical arrangement is unaltered the torsional force will be proportional to the viscosity of the liquid and to the velocity.

A is a metal vessel containing the liquid and surrounded by a thermostat B containing glycerine. Through the bottom of this vessel passes a spindle C to which a pulley is fixed driven by a small motor.

To the top of C is attached the rotating disk E in the centre of which is a jewelled bearing. Above this is the fixed disk separated from it and supported by a hardened steel point resting in the jewelled bearing. A light steel spindle F passing loosely through the metal cover serves to keep the fixed disk parallel to E and to connect it with a torsion measuring device consisting of a spiral steel spring H and an aluminium pointer G which moves over a graduated scale on the metal cover.

Vanes D are also attached to the spindle C which serve to stir the liquid by causing it to rise through vertical channels in the metal cylinder K and to fall over the top of K back into the bath. The bottom of K is bevelled as shown, so that if the liquid contains suspensions these will fall in between the vanes and thus be kept from settling.

The thermostat can be heated by means of the gas ring burner placed below it.

(a) The viscosimeter was calibrated by means of solutions of known viscosity. A 60 per cent. sucrose solution was found exceedingly useful for this purpose, as it gives a wide range of viscosities with temperature change, and the viscosities at various temperatures have been accurately determined by the Bureau of Standards\*.

It was found that the scale deflexions for a given speed of the rotating disk were directly proportional to the viscosity, and also that for a given viscosity the scale deflexions were directly proportional to the speed of the rotating disk over a wide range.

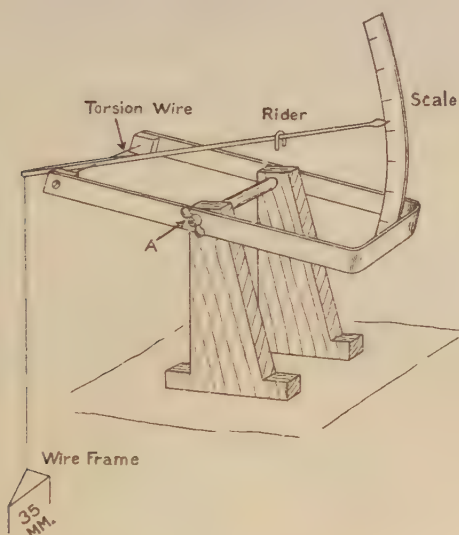
(b) *Surface Tension Apparatus*.—The surface tension apparatus was measured by Wilhelmy's method, viz. by means of the force required to break the film drawn out of

\* E. C. Bingham and R. F. Jackson, Bureau of Standards Bulletin, No. 14, p. 59 (1917).

the liquid by a given length of straight fine wire. If  $l$  is the length of the film,  $f$  the force required to break it, then  $\gamma = \frac{f}{2l}$ . Fig. 3 is a perspective view of this apparatus, which was mounted above the viscosimeter.

A platinum wire frame of the form shown served to pull the film from the liquid, the horns remaining beneath the surface of the liquid until the film broke. This was attached to one end of a light aluminium pointer supported in a metal frame by a torsion wire as shown. This acted as a balance for measuring the force required to break the film.

Fig. 3.



The metal frame could be rotated about an axis through A, thereby raising the platinum wire frame from the surface of the liquid until the film broke. The reading of the pointer could be noted at the moment of breaking and the equivalent force determined by means of a small scale-pan and weights attached to the pointer in place of the wire frame.

The restoring force of the torsion wire could be supplemented by means of a rider attached to the aluminium pointer, so that for a wide range of surface tensions the reading at the break-point could be brought on the scale.



(c) *Drawing Device*.—The fine wires (tungsten or constantan) used as cylinders were cleaned superficially by heating in a reducing atmosphere. They were then wound on a bobbin P (see fig. 2) above the surface of the liquid, and drawn thence round an idle pulley L below the surface of the liquid and finally round the winding bobbin N, which was rotated at a regulated speed. As an approximation to an infinite slab a copper strip about 1 inch wide and 0.05 cm. thick was used. It was thought that if such strip were drawn through the liquid from a bobbin outside it, the liquid might be cooled appreciably when the drawing was rapid. Accordingly the strip was originally wound on a bobbin, wholly immersed in the liquid, and drawn thence direct to the winding bobbin.

(d) *Estimation of thickness*.—The thickness of the layer on the fine wires was determined by weighing a known length of the coated wires on a torsion balance (designed in these Laboratories) capable of estimating a few milligrams with an error of 0.0001 milligram. The coating was then dissolved off and the bare wire weighed. The layer on the strip is uniform only at some distance from the edges; accordingly a known area was cut from the central portion and weighed before and after removal of the layer. The density of the solid layer was determined on a sample of convenient size.

(e) *Liquids used for coating*.—Molten waxes were first used as the liquid for coating the solid surfaces. It was found that filtered beeswax and carnauba wax were most suitable.

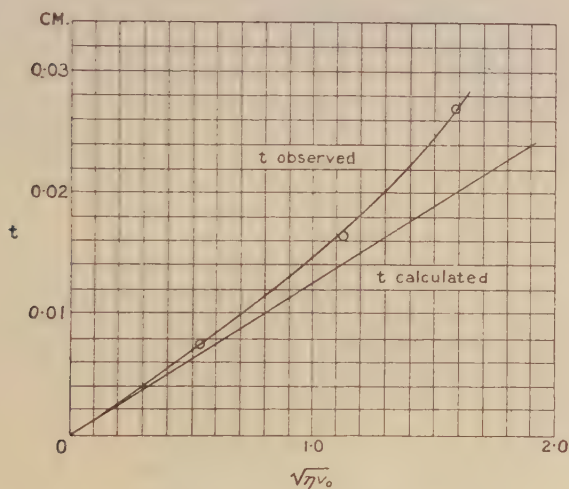
A range of viscosity from 1 to 100 centipoises was obtainable within a temperature range from 50° to 140° C. In some experiments the viscosity was increased by adding fine insoluble powders to form suspensions. Waxes were expected to be particularly advantageous, because their surface tension is low and therefore not likely to be changed by grease and other impurities of low surface tension. But it was found in the course of the work that aqueous solutions could be used with convenience; for by the process of drawing surface impurities were removed very rapidly, so that after a short length had been drawn the surface tension was constant and normal. Some of the observations recorded were made with aqueous solutions of sodium silicate, which were dried on the wire by passing it through a small electric furnace a short distance above the liquid.

## III. Experimental Results.

The results of the experiments on flat strips are shown in fig. 4, where  $t$  {estimated from  $t'$  by (5)} is plotted against  $\sqrt{\eta v_0}$ :  $\eta$  varied from 0.122–0.320 c.g.s. units,  $v_0$  from 2.46–7.85 cm. per sec.,  $\rho$  from 0.8–1.2. The straight line is calculated from (3).

It was pointed out in I. that the assumptions used in the derivation of equation (5) could not be accurately true. Owing to the cooling of the wax, as soon as it leaves the liquid surface its viscosity is increasing, so that it is to be expected that the effective viscosity will be somewhat larger

Fig. 4.



than that measured. The observed thickness of film should therefore be thicker than that calculated on the basis of the measured value, as is actually found.

But the difference is comparatively small; and when it is remembered that (3) involves no empirical constant, but is calculated from measured values only, no doubt will be felt that the theory offered is completely confirmed.

The coating on the edges of the strip was much thinner than on the central portion; it was therefore to be expected that surface-tension effects would be prominent in fine wires. Preliminary measurements on the thickness of the coating on wires of diameter less than 0.02 mm. showed that the coatings were much thinner than were demanded by the theory which takes only gravitation into account (eqn. (7)).

Moreover, it made no difference to the thickness of the coating whether the wire was drawn vertically from the liquid or horizontally through the top of the surface formed by a rotating wheel within the liquid. Surface tension must therefore be the dominant force. This result is in accordance with equ. (9), for the least value of  $\frac{\gamma}{\rho g v_0^2}$  in the observations was 300.

However, the possible effect of instability due to surface tension must be considered. It was clear immediately that the layer originally formed was unstable, for the solidified coating on the wire was not even but was broken up into blobs. These blobs were beautifully symmetrical and evenly distributed when viewed under a microscope. Photomicrographs (1), (2), (3) are shown in fig. 5 (Pl. VIII.). But formation of the blobs evidently occurs after the wire has left the liquid surface; for it does not depend on the velocity of drawing or the viscosity within fairly wide limits. No. (1) was obtained at one-half the speed of No. (2) and at twice the viscosity; in these two cases there is approximately the same thickness of coating. No. 3 was obtained at a higher speed than No. 2, but at the same viscosity. Here the coating is obviously thicker.

That the blobbing took place after the liquid coating had been withdrawn from the liquid was further demonstrated by drawing a wire through glycerine; a very thick film was obtained which remained smooth and even for some inches above the surface of the liquid before it could be seen to break up.

A systematic study of the film thickness as a function of viscosity and surface tension and velocity of drawing as well as the radius of the wire was undertaken.

The following were the limits of the variables :—

Radius of wire  $r=0.00075-0.01$  cm.

Velocity of drawing  $v=5.5-66.0$  cm./sec.

Viscosity  $\eta=1-100$  centipoises.

Surface tension  $\gamma=36-62$  dyne/cm.

Density  $\rho=0.8-1.4$  gm/cm<sup>3</sup>.

The limits of  $v$  and  $\eta$  that could be investigated were set, on the one hand by the impossibility of measuring very thin layers, on the other by the thickness of the film; if  $t$  were greater than  $r_0$  the blobs which formed fell off the wire.

The results are shown in fig. 6 by plotting  $\left(\frac{t}{r_0}\right)$  against  $\left(\frac{\eta v}{\gamma}\right)$ .

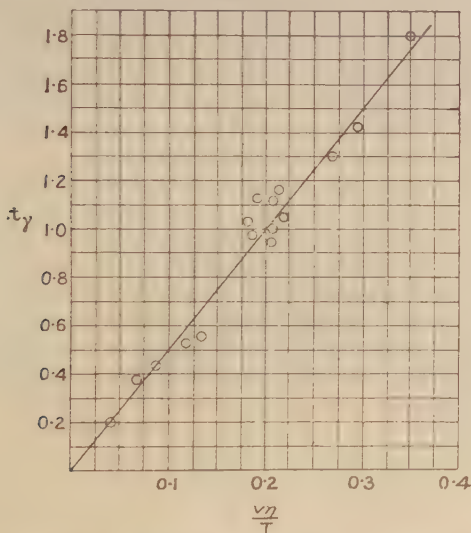
If the theory given is correct, the points should lie on a smooth curve. They do actually lie on such a curve within experimental error, and the curve is seen to be very nearly a straight line. All our measurements on wires can simply be expressed by the formula

$$\frac{t}{r_0} = 4.8 \frac{\eta v}{\gamma}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

the constant 4.8 above being empirical.

It appears, then, that the two extreme cases considered theoretically, namely, all gravity and all surface-tension, are easily realized. Indeed, we have not realized an intermediate case, although it would probably be possible to obtain

Fig. 6.



it with cylinders of greater radius. Further, it appears that there is no special force of 'cohesion' between solid and liquid surfaces which can produce a film even as thick as the thinnest we have examined (0.00007 cm.). If  $r_0$  were infinitely small, *i. e.*, if the surface were allowed to drain for an infinite time, there is no evidence that the film would not be completely removed, or at least reduced to molecular thickness. The only action between solid and liquid important in these experiments is that which prevents slip at the interface. It follows that the coating should be independent of the surface of the solid so long as the liquid wets it at all. As far as our experience goes the conclusion

is correct; *e. g.*, a tungsten wire coated with graphite (from the process of wire-drawing) gave the same results as a clean wire.

In all the experiments described so far the liquids used have been true liquids. But in such processes as enamelling or painting the liquids are usually suspensions. The variation of the viscosity of suspensions with their solid contents and with the size of the suspended particles has been investigated by several authors\*. We have repeated some of this work on liquids in which we were particularly interested, and have confirmed many of their results. But the question arises whether the viscosity of a suspension measured by shearing it between parallel plates is the same as that which determines the amount of liquid adhering to a solid drawn out of it. We have made many observations in this matter. It appears, as might be expected, that the two viscosities are the same so long as the diameter of the suspended particles is not larger than the thickness of the liquid layer drawn out. If the diameter exceeds that thickness the liquid behaves in drawing as if it had a viscosity much less than that measured by shearing. But a consideration of fig. 1 shows that such large particles cannot be expected to enter the layer of liquid on the solid surface; they are squeezed out from it. Accordingly the failure of formula (10) for these large particles is simply due to the fact that the liquid which is being drawn is that from which the large particles have been removed and of which the viscosity is correspondingly lower.

XCI. *On the Distribution of Stresses in a Circular Ring compressed by Two Forces acting along a Diameter.* By S. TIMOSHENKO †.

CONSIDERING the problem as a two-dimensional one, we can obtain a solution in the case represented in fig. 1 by combining the known solutions of the problem of compression of a disk ‡ (fig. 2) and that of a ring § (fig. 3).

If we take the normal and the tangential tensions acting on the inner rim of the ring (fig. 3) as equal and opposite to the tensions acting on the cylindrical surface of the radius  $r$  in a disk (fig. 2), the stress-distribution in the case of

\* E. C. Bingham, *Bur. Stand. Bull.* no. 278 (1916). E. Humphrey and E. Hatschek, *Phys. Soc. Proc.* xxviii, p. 274 (1916).

† Communicated by Prof. E. G. Coker, F.R.S.

‡ See A. E. H. Love, 'Treatise on the Theory of Elasticity,' p. 215, 1920.

§ A. Timpe, *Z. f. Math. u. Phys.* lii, p. 348 (1905).



fig. 1 will be obtained by summing the stresses corresponding to figs. 2 and 3.

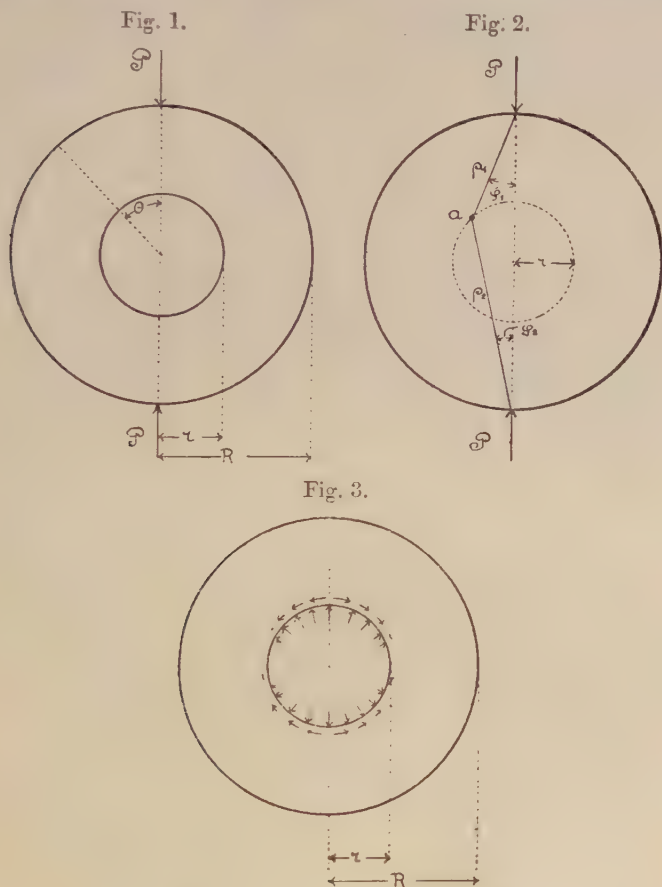


Fig. 4 shows the normal stresses on the vertical and horizontal cross-sections of a ring when  $R=2r$  calculated by the above method. The dotted lines on the same figure represent the results of elementary solutions obtained by using (1) the hypothesis of plane cross-sections or (2) the hypothesis of plane distribution of normal stresses.

The stress-distribution in a compressed disk (fig. 2) is obtained by superposing a tension \*

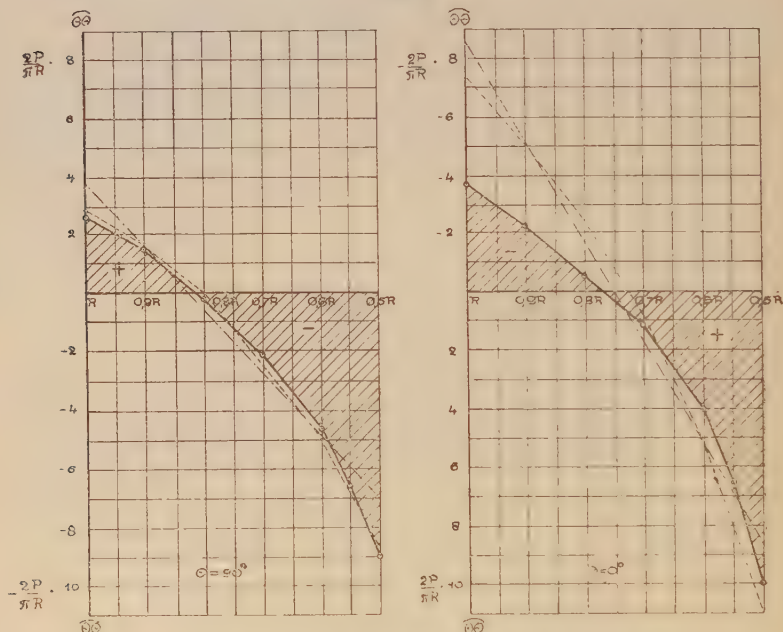
$$\frac{P}{\pi R} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

\* We suppose the thickness of the ring equal to unity,

1016 Prof. S. Timoshenko on the Distribution of  
equal at all points, and two simple radial distributions :

$$-\frac{2P}{\pi} \frac{\cos \phi_1}{\rho_1}, \quad -\frac{2P}{\pi} \frac{\cos \phi_2}{\rho_2} \quad . \quad . \quad . \quad (2)$$

Fig. 4.



If  $R=2r$ , the corresponding normal and tangential stresses at the points of the cylindrical surface of the radius  $r$  will be approximately represented by the following series \* :—

$$\left. \begin{aligned} \widehat{rr} &= -\frac{2P}{\pi R} (0.506 + 1.008 \cos 2\theta + 0.443 \cos 4\theta \\ &\quad + 0.158 \cos 6\theta + 0.0467 \cos 8\theta + 0.0083 \cos 10\theta), \\ \widehat{r\theta} &= \frac{2P}{\pi R} (0.749 \sin 2\theta + 0.374 \sin 4\theta \\ &\quad + 0.141 \sin 6\theta + 0.0460 \sin 8\theta + 0.0133 \sin 10\theta). \end{aligned} \right\} \quad . \quad . \quad (3)$$

Distributing on the inner rim of the ring (fig. 3) the tensions

\* The calculations have been made by the Runge approximate method. See *Theorie und Praxis der Reihen*, p. 153. From the calculations made we may conclude that the error in stresses will not be higher than  $\frac{1}{2}$  per cent. if we take the first six terms of the series only.

which are equal and opposite to the tractions (3), and using the solution of the case of a circular ring, the following expressions are obtained for the stresses at any point :—

$$\begin{aligned} \theta\bar{\theta} = \frac{2P}{\pi R} & \left[ -0.506 \frac{r^2 R^2 + \rho^2}{\rho^2 R^2 - r^2} + \left( 2.268 - 6.324 \frac{\rho^2}{R^2} \right. \right. \\ & + 0.4832 \frac{R^4}{\rho^4} \Big) \cos 2\theta + \left( 0.3691 \frac{\rho^2}{R^2} - 0.6783 \frac{\rho^4}{R^4} \right. \\ & + 0.0368 \frac{R^6}{\rho^6} - 0.0599 \frac{R^4}{\rho^4} \Big) \cos 4\theta + \left( 0.06504 \frac{\rho^4}{R^4} \right. \\ & - 0.10026 \frac{\rho^6}{R^6} + 0.0041319 \frac{R^8}{\rho^8} - 0.00952 \frac{R^6}{\rho^6} \Big) \cos 6\theta \\ & + \left( 0.008758 \frac{\rho^6}{R^6} - 0.01225 \frac{\rho^8}{R^8} + 0.00040795 \frac{R^{10}}{\rho^{10}} \right. \\ & - 0.0010888 \frac{R^8}{\rho^8} \Big) \cos 8\theta + \left( 0.0007880 \frac{\rho^8}{R^8} \right. \\ & - 0.001037 \frac{\rho^{10}}{R^{10}} + 0.00002960 \frac{R^{12}}{\rho^{12}} \\ & \left. \left. - 0.00008475 \frac{R^{10}}{\rho^{10}} \right) \cos 10\theta \right], \end{aligned} \quad (4)$$

$$\begin{aligned} \bar{r}r = \frac{2P}{\pi R} & \left[ 0.506 \frac{r^2 R^2 - \rho^2}{r^2 R^2 - r^2} + \left( -2.268 - 0.4832 \frac{R^4}{\rho^4} \right. \right. \\ & + 2.752 \frac{R^2}{\rho^2} \Big) \cos 2\theta + \left( -0.3691 \frac{\rho^2}{R^2} + 0.2261 \frac{\rho^4}{R^4} \right. \\ & - 0.0368 \frac{R^6}{\rho^6} + 0.1798 \frac{R^4}{\rho^4} \Big) \cos 4\theta + \left( -0.06504 \frac{\rho^4}{R^4} \right. \\ & + 0.05013 \frac{\rho^6}{R^6} - 0.0041319 \frac{R^8}{\rho^8} + 0.01904 \frac{R^6}{\rho^6} \Big) \cos 6\theta \\ & + \left( -0.008758 \frac{\rho^6}{R^6} + 0.007352 \frac{\rho^8}{R^8} - 0.00040795 \frac{R^{10}}{\rho^{10}} \right. \\ & + 0.0018146 \frac{R^8}{\rho^8} \Big) \cos 8\theta + \left( -0.0007880 \frac{\rho^8}{R^8} \right. \\ & + 0.0006911 \frac{\rho^{10}}{R^{10}} - 0.00002960 \frac{R^{12}}{\rho^{12}} \\ & \left. \left. + 0.0001265 \frac{R^{10}}{\rho^{10}} \right) \cos 10\theta \right], \end{aligned} \quad (5)$$

$$\begin{aligned}
 \widehat{r\theta} = \frac{2P}{\pi R} \left[ \left( 2.268 - 3.162 \frac{\rho^2}{R^2} - 0.4832 \frac{R^4}{\rho^4} \right. \right. \\
 + 1.376 \frac{R^2}{\rho^2} \Big) \sin 2\theta + \left( 0.3691 \frac{\rho^2}{R^2} - 0.4522 \frac{\rho^4}{R^4} \right. \\
 - 0.03680 \frac{R^6}{\rho^6} + 0.1198 \frac{R^4}{\rho^4} \Big) \sin 4\theta + \left( 0.06504 \frac{\rho^4}{R^4} \right. \\
 - 0.07520 \frac{\rho^6}{R^6} - 0.0041319 \frac{R^8}{\rho^8} + 0.01428 \frac{R^6}{\rho^6} \Big) \sin 6\theta \\
 + \left( 0.008758 \frac{\rho^6}{R^6} - 0.009802 \frac{\rho^8}{R^8} - 0.00040795 \frac{R^{10}}{\rho^{10}} \right. \\
 + 0.0014517 \frac{R^8}{\rho^8} \Big) \sin 8\theta + \left( 0.0007880 \frac{\rho^8}{R^8} \right. \\
 - 0.0008638 \frac{\rho^{10}}{R^{10}} - 0.00002960 \frac{R^{12}}{\rho^{12}} \\
 \left. \left. + 0.0001054 \frac{R^{10}}{\rho^{10}} \right) \sin 10\theta \right], \quad (6)
 \end{aligned}$$

where  $\rho$  denotes the distance from the centre.

Superposing the stresses (4), (5), (6) on the stresses (1) and (2) above, we obtain the stress-distribution in the compressed ring of fig. 1. The normal stresses on the vertical and horizontal cross-sections of the ring have the following values:—

$$\begin{aligned}
 (\widehat{\theta\theta})_{\theta=0} = \frac{2P}{\pi R} \left[ 0.5 - 0.506 \frac{\rho^2}{R^2} \frac{R^2 + \rho^2}{R^2 - \rho^2} + 2.268 - 5.955 \frac{\rho^2}{R^2} \right. \\
 - 0.6133 \frac{\rho^4}{R^4} - 0.0915 \frac{\rho^6}{R^6} - 0.01146 \frac{\rho^8}{R^8} - 0.00104 \frac{\rho^{10}}{R^{10}} \\
 + 0.4233 \frac{R^4}{\rho^4} + 0.02728 \frac{R^6}{\rho^6} + 0.003043 \frac{R^8}{\rho^8} + 0.0003232 \frac{R^{10}}{\rho^{10}} \\
 \left. + 0.0000296 \frac{R^{12}}{\rho^{12}} \right]; \quad \dots \dots \dots (7)
 \end{aligned}$$

$$\begin{aligned}
 (\widehat{\theta\theta})_{\theta=\frac{\pi}{2}} = \frac{2P}{\pi R} \left[ 0.5 - \frac{2R^4}{(R^2 + \rho^2)^2} - 0.506 \frac{\rho^2}{R^2} \frac{R^2 + \rho^2}{R^2 - \rho^2} - 2.268 \right. \\
 + 6.693 \frac{\rho^2}{R^2} - 0.7433 \frac{\rho^4}{R^4} + 0.1090 \frac{\rho^6}{R^6} - 0.01304 \frac{\rho^8}{R^8} \\
 + 0.001037 \frac{\rho^{10}}{R^{10}} - 0.5431 \frac{R^4}{\rho^4} + 0.04632 \frac{R^6}{\rho^6} - 0.005221 \frac{R^8}{\rho^8} \\
 \left. + 0.0004927 \frac{R^{10}}{\rho^{10}} - 0.00002960 \frac{R^{12}}{\rho^{12}} \right]. \quad \dots \dots \dots (8)
 \end{aligned}$$

The results of these calculations are represented on fig. 4. As a measure of the accuracy of these calculations, we have

$$\int_r^R (\theta\theta)_{\theta=\frac{\pi}{2}} d\rho = -0.5022P, \quad \dots \quad (9)$$

so that the error is smaller than  $\frac{1}{2}$  per cent.

If the corresponding calculations are made for the vertical cross-section, we obtain

$$\int_r^R (\theta\theta)_{\theta=0} d\rho = \frac{P}{\pi} 0.996. \quad \dots \quad (10)$$

This must be compared with the result

$$\int_0^\pi \frac{2P}{\pi} \cos \phi \sin \phi d\phi = \frac{P}{\pi},$$

corresponding to a simple radial distribution (fig. 5). We have again an error smaller than  $\frac{1}{2}$  per cent.

Fig. 5.



The method outlined here may be applied to the more general case of a circular ring subjected to any forces acting on its external rim. It is only necessary to use the corresponding solution for a disk\*.

\* A. E. H. Love, 'Treatise on the Theory of Elasticity,' p. 216.



XCII. *On a Revised Equation of State.* By ALFRED W. PORTER, *D.Sc., F.R.S., F.Inst.P.\**

DIETERICI'S characteristic equation of gases in the reduced form is  $\alpha = \frac{\gamma}{2\beta-1} \exp. \left[ 2\left(1 - \frac{1}{\gamma\beta}\right) \right]$ , which can be modified by putting  $\gamma^n$  instead of  $\gamma$  in the exponential term. This equation is very fairly satisfactory, when  $n=3/2$ , in the region of low pressures; but it breaks down for pressures above the critical value.

Berthelot also developed an equation in which the respective terms are based directly on experiment instead of theory. It is explicitly applicable to low pressures only, and is very much used for that region. This equation is

$$\alpha + \frac{16}{3\gamma\beta^2} = \frac{32\gamma}{\beta - \frac{1}{4}}.$$

It will be observed that it does not pass through the critical point ( $\alpha=\beta=\gamma=1$ ). On fig. 1 are shown experimental values of  $\alpha\beta$  plotted against  $\alpha$  for isopentane, and on this same figure values calculated from Berthelot's equation are represented by a dotted curve. Values from van der Waals' equation are indicated by small squares.

The chief fault of Dieterici's equation is that it makes the critical volume only twice the least volume of the liquid, whereas experiment shows that it is in most cases very nearly four times. To get over this, Dieterici treats the volume of the molecules themselves as being a function of the pressure.

The first object of this paper is to point out that there is a way of testing the equation which shows that this last-stated modification (even if it should be necessary) cannot be the only change required, and that it is no use making it until other changes are made.

If the equation be written

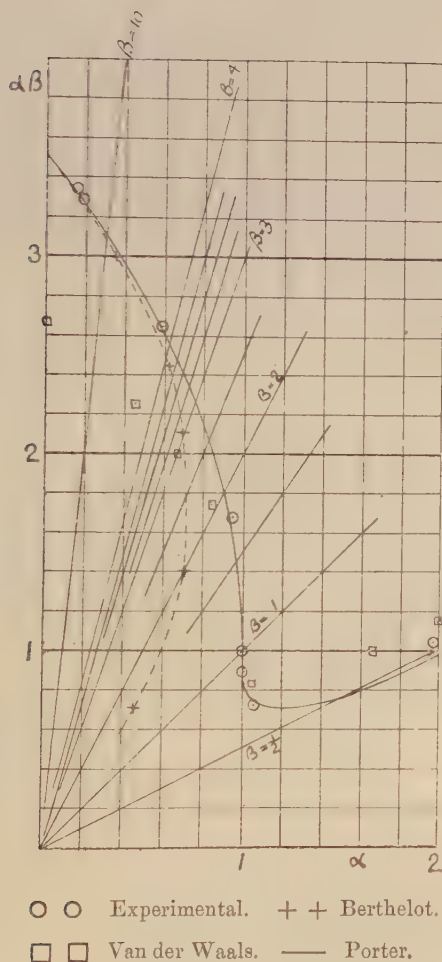
$$\alpha = \gamma F(\beta) \exp. \left( \frac{1}{\gamma^n \beta} \right),$$

where  $F(\beta)$  is a function of the volume alone, the value of

\* Communicated by the Author.

$\frac{\gamma}{\alpha} \frac{\partial \alpha}{\partial \gamma} - 1$  becomes  $-\frac{n}{\gamma^2 \beta}$  whatever the function  $F(\beta)$  may be. Calling this quantity  $l$  (it is connected with the internal

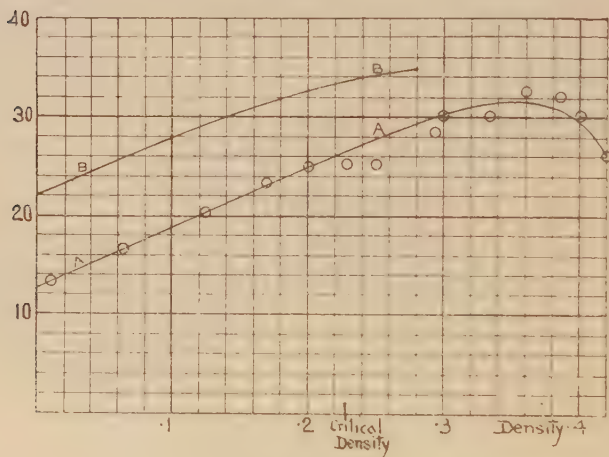
Fig. 1.



latent heat of expansion of the gas per unit change of volume), the value of  $\beta l$  should, according to the Dieterici

equation, be a constant. In fig. 2 are shown two curves of  $\beta l$  plotted against the density ( $1/v$ ) for isopentane determined from the experimental values. Curve A is the critical isotherm and B is the isotherm for  $503^\circ \text{abs.}$  It will be seen from this figure that instead of being constant it undergoes very considerable variation. Near the critical point the calculated points fluctuate, but a smooth curve drawn amongst them shows that an equation of *at least* the second degree is required to represent them.

Fig. 2.



Isopentane.

$\left(T \frac{\partial p}{\partial T} - p\right) \frac{v}{p}$  plotted against Density.

Curve A, Critical Isothermal,  $T = 461 \text{ abs. C.}$

„ B, Isothermal,  $T = 503 \text{ abs. C.}$

If the necessary extra terms are introduced, it becomes possible to bring the equation for the critical isotherm into the form

$$\alpha = \frac{\lambda}{\beta - \frac{1}{4}} \exp. \left[ -\frac{a}{\beta} - \frac{b}{\beta^2} - \frac{c}{\beta^3} \right].$$

The *three* conditions for the critical point are satisfied if

$$\lambda = 3\frac{1}{2}, \quad a = 1.51, \quad b = .267, \quad c = -.237.$$

It is noteworthy that the negative value of  $c$  is required not only from the data of the critical point, but also by the isotherm on fig. 2.

The values of  $a$ ,  $b$ , and  $c$  will be functions of the temperature.

Now 
$$\frac{1}{\alpha\beta} \frac{\partial(\alpha\beta)}{\partial\beta} = \frac{-\frac{1}{4}}{\beta(\beta-\frac{1}{4})} + \frac{a}{\beta^2} + \frac{2b}{\beta^3} + \frac{3c}{\beta^4}.$$

At  $\alpha=0$ ,  $\beta=\infty$ , this becomes zero (and because  $\frac{\partial\alpha}{\partial\beta}$  does not do so, so also does  $\partial(\alpha\beta)/\partial\alpha$ ) when

$$a = \frac{1}{4}.$$

If we write 
$$a = \frac{a_1}{\gamma^n},$$

this occurs when

$$\gamma^n = 4a_1 = 6.04 = (2.455)^2.$$

Now the  $\alpha\beta$  against  $\alpha$  curve for nitrogen starts out horizontally when  $\gamma=2.54$ ; hence  $n=2$  nearly. Inserting these values, which are obtained solely by making the equation suit the critical state, it is interesting to see how nearly the equation becomes Berthelot's equation when the pressure is small. It can be written

$$\alpha = \frac{\frac{7}{2}\gamma}{\beta - \frac{1}{4}} \left( 1 - \frac{1.51}{\gamma^2\beta} + \dots \right),$$

or 
$$\left( \alpha + \frac{5.28}{\gamma\beta^2} \right) = \frac{3.5\gamma}{\beta - \frac{1}{4}} \text{ for large values of } \beta.$$

In Berthelot's equation the numbers are 5.33 and 3.55 respectively.

If  $b$  be written  $b_1/\gamma^m$ , the value of  $m$  is found from the curves of isopentane to be a high one—about 12 to 15. It can be obtained also by considering the value of  $\frac{\partial\alpha}{\partial\gamma}$  at the critical point. We have in general

$$\frac{\gamma\partial\alpha}{\alpha\partial\gamma} = 1 + \frac{na_1}{\gamma^n\beta} + \frac{mb_1}{\gamma^m\beta^2} + \frac{qc_1}{\gamma^q\beta^3},$$

or at the critical point the right side is

$$1 + na_1 + mb_1 + qc_1,$$

or 
$$1 + 3 + .267m - .237q.$$

There are not data enough to find  $m$  and  $q$  with certainty. But since this critical slope is for all substances nearly equal to 7, it follows that  $m$  must be at least 10, which agrees with what we find from the experimental curves.

The critical isotherm calculated from the values of the constants obtained above is shown in fig. 1 as a continuous curve. How nearly it fits the measurements for isopentane down to about  $\frac{1}{2}$  the critical volume is seen by examining the circles which represent experimental points.

The following values given by experiment and also by various equations for the case of  $\beta = \frac{1}{2}$  are useful for comparison to show the success and defect of the revised equation.

Experiment.	Van der Waals.	Dieterici.	Porter.
$\alpha = 2.15$	4	Infinity	1.56
$\alpha\beta = 1.07$	2	Infinity	.782

*XCIII. General Equations of a Balanced Alternating-Current Bridge. By VLADIMIR KARAPETOFF, Professor of Electrical Engineering, Cornell University, Ithaca, N. Y.\**

IN the last few years the use of the Wheatstone bridge for the measurement and comparison of inductances and capacities has considerably increased, partly due to developments in the art of electrical communication, and partly because of improvements in the sources of high-frequency sinusoidal currents. Old classical arrangements of alternating-current bridges have been further developed and new arrangements evolved †. This seems, therefore, to be an opportune time to deduce a general equation of the a.c. bridge which would comprise the various actual bridge arrangements as specific cases. Such a general formula gives a bird's-eye view of the existing bridge connexions and will enable new bridge arrangements to be devised without deducing fundamental equations in each case or constructing vector diagrams. It is hoped that the general formula (D) given below will serve these two purposes.

Some time ago Dr. Poole showed ‡ that the currents and voltages in the usual arrangements of an a.c. bridge, when balanced, can be represented by comparatively simple vector diagrams from which the relationship between the

\* Communicated by the Author.

† See D. I. Cone, "Bridge Methods for Alternating-Current Measurements," *Trans. Amer. Inst. El. Engrs.* vol. xxxix, p. 1743 (1920).

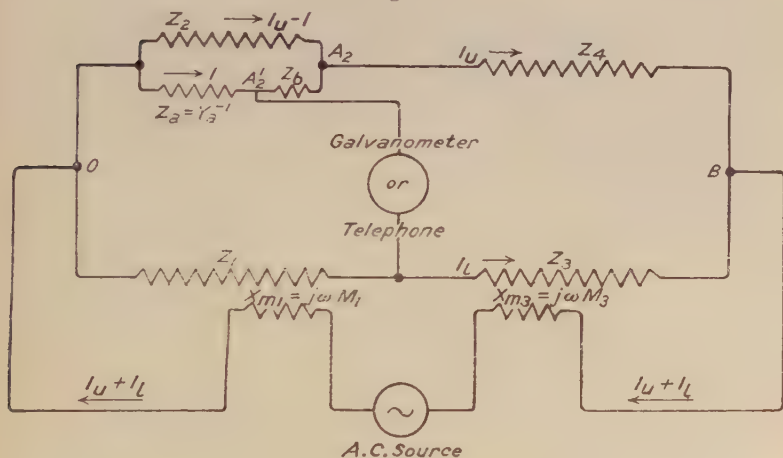
‡ H. H. Poole, "On the Use of Vector Methods in the Derivation of the Formulæ used in Inductance and Capacity Measurements," *Phil. Mag.* vol. xl, p. 793 (1920).



desired quantities can be readily deduced. While his results will be very valuable to the practical users of the bridge, the other side of the problem, that is, a generalization of the theory, may prove to be of interest to investigators of new possibilities of bridge connexions.

Fig. 1 represents general connexions of an a.c. bridge, with an impedance in each branch, and a mutual inductance in each of the lower branches. The upper left-hand branch consists of two paths in parallel, and the galvanometer is connected at an intermediate point,  $A_2'$ , of one of the paths.

Fig. 1.



This is the arrangement used in the so-called Anderson bridge, and is included in the general scheme because of its further possibilities. The bridge is supposed to be balanced on alternating current, that is, the galvanometer current is supposed to be equal to zero.

The current in the lower branches is denoted by  $I_l$ , that in the upper branches by  $I_u$ . In the divided branch 2 the current through the lower path is denoted by  $I$ , so that the current through the other path is  $I_u - I$ . The line current is  $I_u + I_l$ . The impedances  $Z$  in the two left-hand branches are denoted with the subscripts 1 and 2, to agree with the sketches in Dr. Poole's article. The right-hand quantities are provided with the subscripts 3 and 4, although Dr. Poole uses again the subscripts 1 and 2, except in his fig. 5, where the subscript 4 is introduced in the same place as in this article.

Assuming the currents and the impedances to be expressed as complex quantities, we have the following three fundamental equations of the voltage drop in the parts of the bridge:—

$$I_l Z_1 - (I_u + I_l) X_{m1} = I Z_a \quad . \quad . \quad . \quad (A)$$

$$I Z_b + I_u Z_4 = I_l Z_3 - (I_u + I_l) X_{m2} \quad . \quad . \quad (B)$$

$$(I_u - I) Z_2 = I (Z_a + Z_b) \quad . \quad . \quad . \quad (C)$$

Eliminating the currents from these equations, we obtain the following *general relationship among the impedances of a balanced bridge*:—

$$(Z_3 - X_{m3}) [(Z_2 + X_{m1}) + Y_a X_{m1} (Z_2 + Z_b)] = (Z_1 - X_{m1}) [(Z_4 + X_{m3}) (1 + Y_a (Z_2 + Z_b)) + Y_a Z_2 Z_b] \quad . \quad (D)$$

In this equation the admittance  $Y_a$  is used in place of the impedance  $Z_a$ ; the relationship between the two is  $Z_a Y_a = 1$ .

While in any special case eq. (D) may be applied directly, there are some typical special cases for which it is more convenient to write simplified forms of eq. (D). Eight such cases are considered below.

(1) *No mutual inductances and a single-path branch 2.* This means that  $X_{m1} = X_{m3} = 0$ , and  $Y_a = 0$ ; we then have a simple bridge consisting of four impedances. Eq. (D) becomes

$$Z_3 Z_2 = Z_1 Z_4 \quad . \quad . \quad . \quad (1)$$

(2) *No mutual inductance and a single-shunt branch 2.* Here again  $X_{m1} = X_{m3} = 0$  and  $Z_b = 0$ . The points  $A_2$  and  $A_2'$  coincide, and  $Z_a$  is in parallel with  $Z_2$ . Eq. (D) becomes

$$Z_3 Z_2 = Z_1 Z_4 (1 + Y_a Z_2) \quad . \quad . \quad . \quad (2)$$

(3) *No mutual inductance and a double shunt in branch 2,* as shown in fig. 1. In this case the only simplification is that  $X_{m1} = X_{m3} = 0$ , and eq. (D) gives

$$Z_3 Z_2 = Z_1 [Z_4 (1 + Y_a (Z_2 + Z_b)) + Y_a Z_2 Z_b] \quad . \quad . \quad (3)$$

(4) *Mutual inductance in branch 3 only and no shunt in branch 2.* We have  $X_{m1} = 0$  and  $Y_a = 0$ ; eq. (D) becomes

$$(Z_3 - X_{m3}) Z_2 = Z_1 (Z_4 + X_{m3}) \quad . \quad . \quad . \quad (4)$$

(5) *Mutual inductance in branch 3 only and a single shunt in branch 2.* In this case  $X_{m1} = Z_b = 0$  and  $Z_a$  is in parallel with  $Z_2$ . Eq. (D) gives

$$(Z_3 - X_{m3}) Z_2 = Z_1 [(Z_4 + X_{m3}) (1 + Y_a Z_2)] \quad . \quad . \quad (5)$$

(6) *Mutual inductance in branch 1 only and no shunt in branch 2.* We have  $X_{a3}=0$  and  $Y_a=0$ ; eq. (D) becomes

$$Z_3(Z_2 + X_{m1}) = (Z_1 - X_{m1})Z_4 \quad . \quad . \quad . \quad (6)$$

(7) *Mutual inductance in branch 1 only and a single shunt in branch 2.* In this case  $X_{m3}=Z_b=0$  and  $Z_a$  is in parallel with  $Z_2$ . Eq. (D) gives

$$Z_3[(Z_2 + X_{m1}) + Y_a X_{m1} Z_2] = (Z_1 - X_{m1})(1 + Y_a Z_2)Z_4 \quad . \quad (7)$$

(8) *Mutual inductance in both branches, but the branch 2 is not shunted.* In this case  $Y_a=0$ , and eq. (D) becomes

$$(Z_3 - X_{m3})(Z_2 + X_{m1}) = (Z_1 - X_{m1})(Z_4 + X_{m3}). \quad . \quad (8)$$

In the following table the special applications of the bridge are those discussed by Dr. Poole in the article mentioned above, and the references are to the figures in his article. All these applications are covered by the foregoing eight special cases of formula D, and the case number is stated for each application. In some applications the four resistances of the bridge have first to be balanced with direct current, in other cases it is not feasible. This is indicated by "yes" or "no" in one of the columns.

It will now be shown how readily the familiar formulæ for the measurements shown in the table can be derived from the formulæ (1) to (8), all of which are specific cases of eq. (D). The item numbers below refer to the items in the table, and in each case an equation is used as indicated in the table. All the results check with those given by Dr. Poole.

*Item No. 1:*

$$(r_3 + j\omega L_3)r_2 = r_1(r_4 + j\omega L_4).$$

Separating the real and the imaginary parts, gives

$$r_3 r_2 = r_1 r_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$L_3 r_2 = r_1 L_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

These equations combined give

$$L_3/L_4 = r_1/r_2 = r_3/r_4 \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Eq. (9) shows that the bridge must be balanced on direct current as well as on alternating current.

Item No.	By whom originated.	Quantities to be compared or measured.	Poole's Fig. No.	Direct Current Balance.	Case of eq. (D).	$Z_1$ .	$Z_2$ .	$Z_3$ .	$Z_4$ .	$Y_a$ .	$Z_b$ .	$X_{m1}$ .	$X_{m3}$ .
1.	Maxwell.	Two self-inductances.	1	yes	1	$r_1$	$r_2$	$r_3 + j\omega L_3$	$r_4 + j\omega L_4$	...	...	$j\omega M_1$	$X_{m3}$ .
2.	Maxwell.	Two mutual inductances.	2	no	8	$r_1 + j\omega L_1$	0	$r_3 + j\omega L_3$	0	...	...	$j\omega M_1$	$j\omega M_3$
3.	Maxwell.	Mutual and self-inductance.	3	yes	4	$r_1$	$r_2$	$r_3 + j\omega L_3$	$r_4 + j\omega L_4$	...	...	$j\omega M_1$	$j\omega M_3$
4.	De Sauty.	Two capacities.	4	no	1	$r_1$	$r_2$	$-j/\omega C_3$	$-j/\omega C_4$	...	...	...	...
5.	Anderson.	Self-inductance and capacity ( $r_b = 0$ ).	5	yes	2	$r_1$	$r_2$	$r_3 + j\omega L_3$	$r_4$	$j\omega C_a$	0	...	...
6.	Anderson.	Self-inductance and capacity ( $r_b > 0$ ).	5	yes	3	$r_1$	$r_2$	$r_3 + j\omega L_3$	$r_4$	$j\omega C_a$	$r_b$	...	...
7.	Carey Foster.	Mutual inductance and capacity.	6	no	6	$r_1 + j\omega L_1$	0	$r_3 + j\omega C_3$	$r_4$	...	...	$j\omega M_1$	...
8.	Matheson-Cone.	Frequency.	...	no	2	$r_1 - j/(\omega C_1)$	$r_2$	$r_3$	$r_4$	$j\omega C_a$	$r_b$	...	...

Item No. 2 (see Note at the end) :

$$(r_3 + j\omega L_3 - j\omega M_3) j\omega M_1 = (r_1 + j\omega L_1 - j\omega M_1) j\omega M_3,$$

from which

$$L_3 M_1 = L_1 M_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\text{and} \quad r_3 M_1 = r_1 M_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

These equations, combined, give

$$M_1/M_3 = L_1/L_3 = r_1/r_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The bridge cannot be balanced on direct current, but the ratio of the resistances must be equal to that of the self-inductances, before two mutual inductances can be compared.

Item No. 3 :

$$(r_3 + j\omega L_3 - j\omega M_3) r_2 = r_1 (r_4 + j\omega L_4 + j\omega M_3).$$

$$\text{Consequently} \quad r_3 r_2 = r_1 r_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$r_2 (L_3 - M_3) = r_1 (L_4 + M_3) \quad . \quad . \quad . \quad . \quad (16)$$

so that

$$r_1/r_2 = r_3/r_4 = (L_3 - M_3)/(L_4 + M_3) \quad . \quad . \quad . \quad (17)$$

Item No. 4 :

$$-jr_2/\omega C_3 = -jr_1/\omega C_4.$$

$$\therefore \quad r_2 C_4 = r_1 C_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Item No. 5 :

$$(r_3 + j\omega L_3) r_2 = r_1 r_4 (1 + jr_2 \omega C_a),$$

from which

$$r_3 r_2 = r_1 r_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$L_3 = r_1 r_4 C_a \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Item No. 6.

$$r_2 (r_3 + j\omega L_3) = r_1 [r_1 (1 + j\omega C_a (r_2 + r_b)) + j\omega C_a r_2 r_b].$$

Equating the real and the imaginary parts, we get

$$r_2 r_3 = r_1 r_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$r_2 L_3 = r_1 C_a [r_1 (r_2 + r_b) + r_2 r_b] \quad . \quad . \quad . \quad (22)$$

or, combining the two,

$$L_3 = C_a [r_1 r_4 + r_b (r_1 + r_3)] \quad . \quad . \quad . \quad . \quad (23)$$

When  $r_b = 0$ , this expression becomes identical with eq. (20).

Item No. 7 :

$$(r_3 - j/\omega C_3) j\omega M_1 = (r_1 + j\omega L_1 - j\omega M_1) r_4.$$



Separating the real and the imaginary parts, we get

$$M_1/C_3 = r_1 r_4 \quad . \quad . \quad . \quad . \quad . \quad (24)$$

and

$$r_3 M_1 = (L_1 - M_1) r_4 \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Eq. (25) may be also written in the form

$$L_1/M_1 = 1 + (r_3/r_4) \quad . \quad . \quad . \quad . \quad . \quad (25 a)$$

Item No. 8. This frequency bridge was described by Mr. Cone, *ibid.* p. 1749. Eq. (2) gives:—

$$r_3 r_2 = r_4 [r_1 - j/(\omega C_1)] (1 + j\omega C_2 r_2) \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Separating the real and the imaginary parts, we get

$$r_3 r_2 / r_1 = r_1 + C_2 r_2 / C_1 \quad . \quad . \quad . \quad . \quad . \quad (27)$$

$$1/(\omega C_1) = \omega C_2 r_1 r_2 \quad . \quad . \quad . \quad . \quad . \quad (28)$$

The last equation gives

$$\omega^2 C_1 C_2 r_1 r_2 = 1 \quad . \quad . \quad . \quad . \quad . \quad (29)$$

from which the unknown frequency may be computed. The following special case is of practical interest. In eq. (27) put  $r_3 = r_1$  and  $r_2 = 2r_1$ ; then  $C_1 = 2C_2$ , and eq. (29) becomes

$$\alpha C_1 r_1 = \omega C_2 r_2 = 1 \quad . \quad . \quad . \quad . \quad . \quad (30)$$

As is mentioned above, the general equation (D), or any of its particular forms, (1) to (8), may be used for the derivation of new forms of the bridge. Take for example the simplest case, that of eq. (1). It may be written in the form

$$(r_3 + jx_3)(r_2 + jx_2) = (r_1 + jx_1)(r_4 + jx_4) \quad . \quad . \quad . \quad (31)$$

Separating the real and the imaginary parts, we get

$$r_3 r_2 - x_3 x_2 = r_1 r_4 - x_1 x_4 \quad . \quad . \quad . \quad . \quad . \quad (32)$$

$$x_3 r_2 + r_3 x_2 = x_1 r_4 + r_1 x_4 \quad . \quad . \quad . \quad . \quad . \quad (33)$$

We may put, if we so choose,  $r_3 r_2 = r_1 r_4$ , that is, require the bridge to be first balanced with direct current. Then eq. (32) becomes  $x_3 x_2 = x_1 x_4$ , and these two conditions, together with eq. (33), may be used to investigate various possible bridge combinations with resistances and inductances. The condition  $r_3 r_2 = r_1 r_4$  may be dropped and eqs. (32) and (33) used for an investigation of various bridge arrangements containing resistance, inductance, and capacity. One or two of the  $x$ 's may be put equal to zero, with a resulting simplification in the algebraic relationships. In a similar manner, eqs. (2) to (8) may be resolved into their

component parts and the possibilities of various bridge connexions and measurements analysed, using only elementary algebraic transformations.

When one or more branches of a bridge contain parallel paths, quicker results may be obtained by using admittances in place of impedances. Let, for example, the branches 1 and 4 contain ohmic resistances only, let branch 3 contain an impedance  $r_3 + j\omega L_3$ , and let branch 2 consist of a capacitive susceptance  $j\omega C_a$  in parallel with a resistance  $r_2$ . We then have, according to eq. (1),

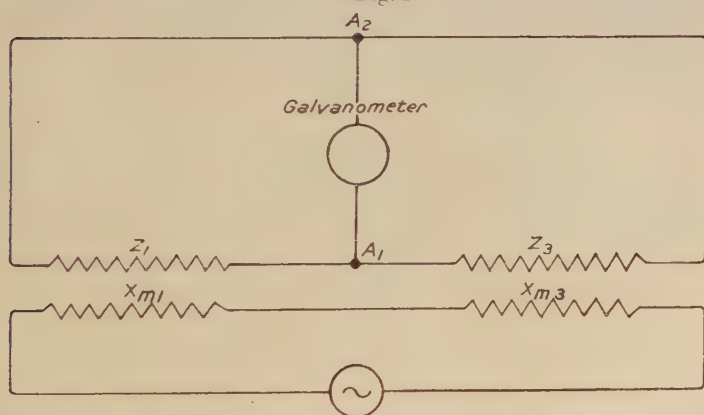
$$(r_3 + j\omega L_3) / \left( \frac{1}{r_2} + j\omega C \right) = r_1 r_4 \quad . \quad . \quad . \quad (34)$$

or

$$r_3 + j\omega L_3 = r_1 r_4 / r_2 + j\omega r_1 r_4 C_a \quad . \quad . \quad . \quad (35)$$

Equating the real and the imaginary parts, eqs. (19) and (20) are obtained.

Fig. 2.



*Note.*—Fig. 2 shows the diagram of connexions of Maxwell's mutual inductance bridge (item 2 in the table). At first sight it does not seem possible that fig. 2, with its two separate circuits, could be a particular case of fig. 1 which has one circuit only. In order to explain the transformation of fig. 1 into fig. 2, intermediate diagrams of connexions are shown in figs. 3 and 4. In fig. 3, the impedances  $Z_2$  and  $Z_4$  are assumed to be very small, otherwise the connexions are the same as in fig. 1 for the case of a single path in branch 2. In other words, the points O, B, and  $A_2$  are electrically close to each other. In fig. 4 the limiting assumption is made that  $Z_2 = Z_4 = 0$ , and the three points are brought together. Under these conditions

no current can flow from the primary into the secondary circuit by *conduction*, since the two circuits have only one point in common. The secondary current is produced only by *induction*, and the two circuits may just as well be entirely separate. In this manner fig. 2 is obtained from fig. 4.

Fig. 3.

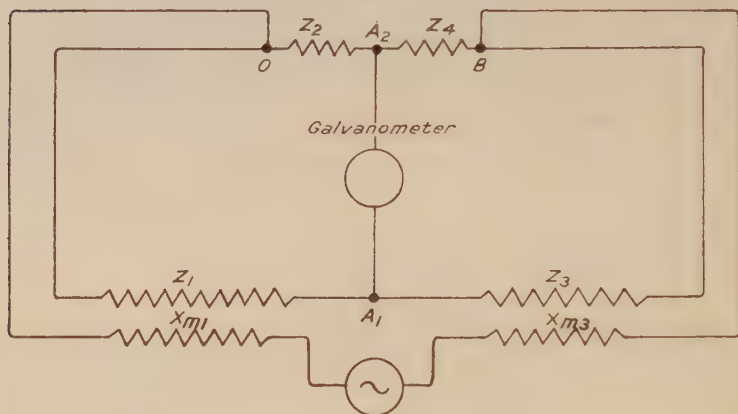
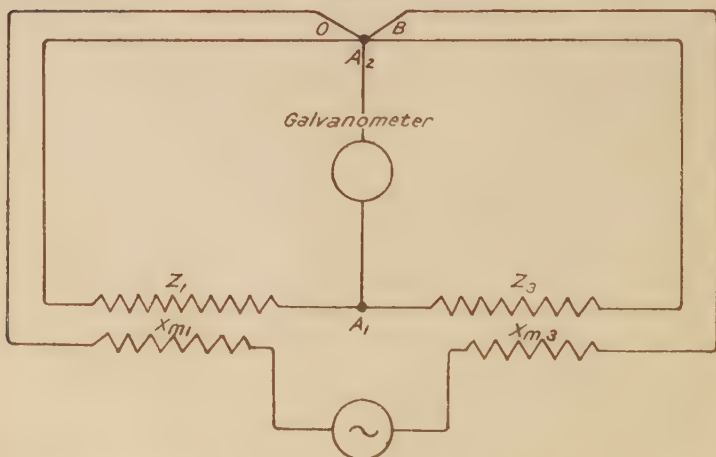


Fig. 4.



This also explains the reason for which  $Z_2$  and  $Z_4$  in the table are marked equal to zero. Thus, the fundamental formula (D) is also applicable to bridges in which the secondary current is produced entirely by mutual induction, and the primary source of current has no metallic connexion with the bridge itself.

XCIV. *The Motion of Electrons in Argon and in Hydrogen.*  
 By J. S. TOWNSEND, M.A., F.R.S., Wykeham Professor  
 of Physics, Oxford, and V. A. BAILEY, M.A., The Queen's  
 College, Oxford\*.

1. **T**HE experiments on the motion of electrons in argon which we have already published show such remarkable differences between this gas and nitrogen or hydrogen, that we considered it desirable to make further experiments with argon which had been very completely purified, and to extend the determinations of the velocities over larger ranges of pressures and forces.

For this purpose it was necessary to construct an apparatus suitable for measuring the velocity in the direction of the electric force, and also the velocity of agitation when the electrons move in a widely diverging stream after passing through a narrow slit in a metal sheet.

In order to obtain accurate results it is necessary in all cases that the gas should be free from impurities which tend to form ions. With gases like argon, where the electron loses a very small proportion of its energy in colliding with a molecule, the gas should be free not only from impurities that tend to form ions but also from gases like nitrogen and hydrogen, as the loss of energy of an electron in a collision with a molecule of one of these gases, although small, is large compared with the loss of energy in a collision with argon. Also the effect of such impurities in argon is accentuated by the fact that the probability of a collision between an electron and a molecule is much greater in the other gases than in argon.

It was found that impurities get into the gases from the materials such as ebonite or elastic cement generally used in the construction of apparatus for measuring velocities, so that in nitrogen or hydrogen the results obtained after the gas had been in the apparatus for a few days were slightly different from those obtained immediately after the gas had been admitted. In the case of argon the effect of these impurities was noticeable after the gas had been in the apparatus for one day.

2. In order to eliminate the impurities emanating from the apparatus, glass was used instead of ebonite to insulate and fix in position the various electrodes and guard-rings, and the connexions were made through glass capillary tubes instead of ebonite plugs. The capillary tubes were slightly

\* Communicated by the Authors.

tapered and ground to fit into metal sockets in the outer case of the instrument, the wax used for sealing being applied only on the outside of the joint. A great improvement was thus obtained, and two instruments of different dimensions were constructed, one with a slit 2 centimetres from the receiving electrodes suitable for measuring velocities in gases like argon where the lateral diffusion of a stream of electrons is very wide, and the other similar to that which had been previously used with the slit 4 centimetres from the receiving electrodes. When tested with hydrogen no change was observed in the velocities after the gas had been in the apparatus for several days, and with pure argon the changes in two or three days were extremely small.

In the instrument with the slit 2 centimetres from the receiving electrodes the guard-rings and the electrodes were fixed in the positions shown in fig. 1. The electrons are set free from the copper plate P by ultraviolet light admitted through a quartz plate sealed in the cover of the instrument, and the stream of electrons that passes through the gauze G and the slit S is received by the electrodes  $E_1$ ,  $E_2$ , and  $E_3$ . These electrodes were mounted on two strips of plate glass fixed to the guard-ring  $R_1$ , so that the upper surfaces of the electrodes were in the same plane with the upper surface of the ring. The ring  $R_1$  was 7.8 centimetres internal diameter and 11.6 centimetres external diameter, and was at zero potential. The ring  $R_2$ , of the same size as  $R_1$ , was insulated and fixed at a distance of one centimetre from  $R_1$ . The slit S was 2 millimetres wide and 1.5 centimetres long in a sheet of silver foil stretched inside the brass ring A, and fixed at a distance of 2 centimetres from the receiving electrodes. The gauze of silver wire G was at a distance of 3 centimetres and the plate P at a distance of 6 centimetres from the receiving electrodes. A uniform electric field was obtained by maintaining the ring  $R_2$ , the plate A, and the gauze G at potentials V, 2V, and 3V proportional to their distances from the receiving electrodes E. In most of the experiments the plate P was maintained at the potential 6V, and the electric force from this plate to the gauze was the same as the force in the lower part of the field. The object of the gauze was to ensure that the electrons should have attained the steady state of motion corresponding to the force Z in the lower part of the field before passing through the slit. This condition may be obtained without the gauze by fixing the plate P at the potential 6V, and for experiments with gases at low pressures this gauze is unnecessary. But with large pressures above 20 or 30 millimetres the currents become



very small when the electric force is small and the plate P is at the potential 6V. The current is increased by increasing the potential of the plate P, and with the gauze at the potential 3V the electrons pass through a distance of one centimetre under the force Z before reaching the slit. With the gases at the higher pressures the number of collisions of each electron with molecules of the gas in this distance is very large, and the motion of the electron acquires the steady state corresponding to the force Z before passing through the slit.

Fig. 1

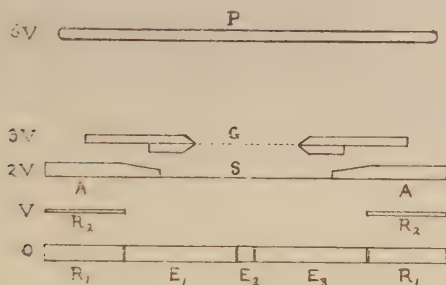
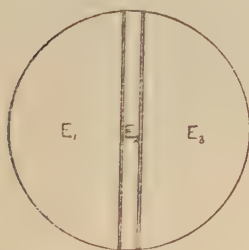


Fig. 2.



In the instrument with the slit 4 centimetres from the receiving electrodes there are three guard-rings between R<sub>1</sub> and the ring A with the slit, as shown in the diagram, page 875, Phil. Mag. Dec. 1921. The dimensions of the electrodes and the guard-rings were the same in both instruments.

In order to avoid errors which might arise from contact potentials at the surfaces of the rings R or the electrodes E, the metal surfaces were all electroplated with silver which is less liable to become oxidized than brass. The variations in contact potential which may arise owing to oxidation

would be too small to have an appreciable effect in most of the experiments as the electric forces were so large, but it was considered advisable to reduce as far as possible any error that might affect the experiments with the smaller forces.

In the original apparatus the electrodes were of unsilvered brass, and when the experiments with hydrogen were repeated with the silvered electrodes almost exactly the same results were obtained.

3. The position of the slit in both instruments was adjusted to bring the centre of the stream slightly to one side of the centre of the electrode  $E_2$ . This arrangement makes the instruments very adaptable for the measurement of the velocities in the direction of the electric force.

For this purpose the stream is deflected by a transverse magnetic force  $H$  which is adjusted to bring the centre of the stream to coincide with one of the gaps between  $E_2$  and the electrodes  $E_1$  and  $E_3$ . The electrode  $E_2$  was a flat strip 4.5 millimetres wide and each of the gaps .5 millimetre wide, so that the distance between the centres of the two gaps was 5 millimetres. Let this distance be  $2a$ ,  $b$  the distance of the centre of the stream from the centre of the electrode  $E_2$  when  $H=0$ ,  $H_1$  the magnetic force required to deflect the centre of the stream through the distance  $a+b$ , so that the current received by  $E_1$  is equal to that received by  $E_2$  and  $E_3$ ,  $H_3$  the magnetic force in the opposite direction which deflects the centre through the distance  $(a-b)$ , the current received by  $E_3$  being then equal to that received by  $E_2$  and  $E_1$ . The velocity  $W$  in the direction of the electric force  $Z$  is given by the equations

$$\frac{H_1 W}{Z} = \frac{a+b}{c}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{H_3 W}{Z} = \frac{a-b}{c}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $c$  is the distance from the slit to the electrodes  $E$ . Thus  $b$  is determined by the relation  $H_1/H_3 = (a+b)/(a-b)$ .

The magnetic field which was uniform in the space between the slit and the electrodes  $E$  was produced by a current in two large coils fixed in position on either side of the apparatus. With the larger gas pressures the velocities  $W$  are comparatively small, and it was convenient to deflect the stream through the shorter distance  $a-b$  as the coils became overheated when currents of the order of 15 amperes

were flowing through them during the time required to make the observations. The distance  $b$  was found with the gas at one of the lower pressures when the velocities were large, and comparatively small currents were required to obtain either the deflexion  $(a+b)$  or  $(a-b)$ . This method was found quite satisfactory with nitrogen or hydrogen in the second instrument where the slit was 4 centimetres from the receiving electrodes, and the distance  $b=6$  millimetre.

4. With the first instrument where the slit was 2 centimetres from the receiving electrodes, it would have been necessary to double the magnetic forces in order to produce similar deflexions. In this case the following method was used to measure the velocities in argon at the higher pressures. When the centre of the stream is at a distance  $b$  to the right of the electrode  $E_2$  (figs. 1 & 2), the current received by  $E_3$  is larger than that received by  $E_1$ . By means of a suitable magnetic force  $H_2$  the centre of the stream may be deflected through the distance  $b$  and thus brought to the centre of  $E_2$ . The two electrodes  $E_1$  and  $E_3$  then receive equal charges. The value of  $H_2$  was found by measuring these two charges with the central electrode maintained at zero potential, and adjusting the magnetic force to the point at which the charges are equal.

The velocity  $W$  is then given by the equation

$$\frac{H_2 W}{Z} = \frac{b}{c} \cdot \cdot \cdot \cdot \cdot \cdot (3)$$

In order to find  $b$ , the stream is deflected in the opposite direction through the distance  $(a-b)$ , which is attained when the current received by  $E_1$  and  $E_2$  is equal to that received by  $E_3$ , the required magnetic force  $H_3$  being given by equation (2). Thus  $b$  is given by the relation  $H_2/H_3=b/(a-b)$ , and was found to be .87 millimetre.

In argon at the higher pressures the velocities  $W$  were found by this method, and the currents necessary to produce the magnetic fields  $H_2$  were from 10 to 15 amperes.

These results were tested by finding the velocities of electrons in hydrogen with both instruments. The hydrogen was admitted through palladium tubes sealed in the apparatus, and the experiments were made with different forces  $Z$  and pressures  $p$ , the ratio of the force to the pressure being varied from the value  $Z/p=.2$  to  $Z/p=40$ . There was a close agreement between the results obtained with the two instruments.

The velocities obtained for the different values of the ratio

$Z/p$  were on an average less by about 2 per cent. than those obtained in the previous experiments \* with hydrogen.

5. The velocity of agitation  $u$  of the electrons is deduced from measurements of the ratio of the charge received by the central electrode  $E_2$  to the sum of the charges received by the electrodes  $E_1$ ,  $E_2$ , and  $E_3$ .

The theory of the method has already been explained † in detail, and may be expressed briefly as follows:—When a stream of electrons moves under an electric force, the number per cubic centimetre at any point is a function of the quantity  $eZ/mu^2$  when the steady state corresponding to the force  $Z$  is attained,  $e$  being the atomic charge,  $Z$  the electric force and  $mu^2/2$  the energy of agitation of the electrons. If  $M\Omega^2/2$  be the energy of agitation of a molecule of a gas at  $15^\circ\text{C}$ ., the velocity of agitation  $u$  of an electron would be  $1.15 \times 10^7$  cm. per sec. if its energy of agitation were equal to  $M\Omega^2/2$ . When moving under an electric force the energy of agitation of the electron is much greater than this quantity, and if  $mu^2 = kM\Omega^2$  the quantity  $eZ/mu^2$  becomes  $eZ/kM\Omega^2$ . This ratio may be written  $NeZ/kNM\Omega^2$ , where  $N$  is the number of molecules per cubic centimetre of a gas at 760 mm. pressure and  $15^\circ\text{C}$ .; and since the quantities  $Ne$  and  $NM\Omega^2$  are known accurately, the number of electrons per cubic centimetre at any point of the stream is a function of  $Z/k$  and known constants.

The ratio  $R = n_2/(n_1 + n_2 + n_3)$  of the charge  $n_2$  received by the central electrode  $E_2$  to the sum of the charges  $n_1$ ,  $n_2$ ,  $n_3$  received by the three electrodes  $E_1$ ,  $E_2$ ,  $E_3$  may therefore be expressed in terms of the ratio  $Z/k$ , and the values of  $R$  corresponding to definite values of  $Z/k$  may be computed. The value of  $R$  for any value of  $Z/k$  may be represented by means of a curve, the form of the curve depending on the sizes of the receiving electrodes and the size and position of the slit.

It was necessary therefore to calculate the values of  $R$  for different values of  $Z/k$  when the centre of the stream fell to one side of the centre of the electrode  $E_2$  with the slit two and four centimetres from the electrodes  $E$ . As it is difficult to construct the apparatus so that the displacement  $b$  of the centre of the stream from the centre of  $E_2$  is some exact fraction of a millimetre, the points on four curves were calculated which are given in fig. 3.

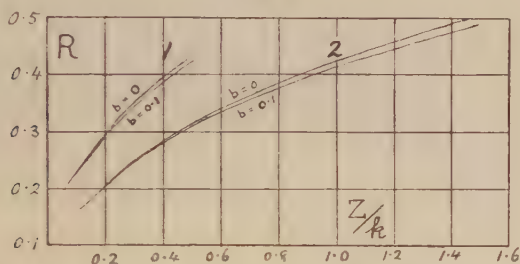
The curves 1 give  $R$  for receiving electrodes of the dimensions shown in figs. 1 and 2, with the slit two centimetres

\* Phil. Mag. Dec. 1921.

† J. S. Townsend, Proc. Roy. Soc. A, lxxxi. p. 464 (1908).

from the plane of the electrodes, the upper curve corresponding to the case where the centre of the stream falls on the centre of  $E_2$  ( $b=0$ ) and the lower curve where the centre of the stream is one millimetre from the centre of  $E_2$  ( $b=.1$ ). The curves 2 give the value of  $R$  under the same conditions, except that the slit is four centimetres from the receiving electrodes. In each case the curves for  $b=0$  and  $b=.1$  are close together, and the correct ratio  $R$  for any intermediate value of  $b$  is easily estimated.

Fig. 3.



The method adopted for calculating the ratios  $R$  corresponding to definite values of  $Z/k$  was similar to that used by Mackie \* to find the points on the curve 2 ( $b=0$ ).

In the course of the calculations we redetermined the points on this curve and obtained numbers almost exactly the same as those given by Mackie.

The calculated values of  $R$ , from which the curves were drawn, are given in Table I.

TABLE I.

$\frac{Z}{k}$	R.			
	$c=2.$		$c=4.$	
	$b=0.$	$b=.1.$	$b=0.$	$b=.1.$
.05	.196	.195	—	—
.1	.231	.230	.1607	.1602
.2	.298	.295	.2077	.2066
.3	.353	.348	.2495	.2476
.4	.397	.389	—	—
.5	.435	.425	.314	.310
1	—	—	.425	.415
1.5	—	—	.506	.490
2	—	—	.570	.548
2.5	—	—	.619	.590

\* J. H. Mackie, Proc. Roy. Soc. A, xc. p. 69 (1914).



If the ratio  $R = n_2 / (n_1 + n_2 + n_3)$  be determined experimentally when the stream is moving under an electric force  $Z$ , the value of  $Z/k$  corresponding to  $R$  is given by the curves (fig. 3), and the factor  $k$  is thus found. The velocity of agitation  $u$  of the electrons is then given by the formula  $u = 1.15 \times 10^7 \times \sqrt{k}$ . None of the experiments were made with the ratio  $R$  less than .24, as greater accuracy is obtained with the larger ratios.

6. The accuracy of the normal distribution curves was tested by measuring the velocities of agitation of the electrons in hydrogen with each instrument. The experiments were made over the same range of forces and pressures as the test experiments on the velocities in the direction of the electric force. The values of  $k$  obtained with the two instruments were in very close agreement, and on an average they did not differ by more than 2 per cent. from the values of  $k$  found in the previous experiments.

It may be mentioned that in the previous experiments the hydrogen was prepared by the electrolysis of barium hydrate, and passed over hot copper into a drying-flask, from which it was admitted through a tap into the apparatus. In the test experiments with the new instruments the hydrogen was admitted through a palladium tube without bringing the gas into contact with any chemicals from which an impurity might have been given off. There was no leak in either instrument which could be detected by means of a McLeod gauge, even when the apparatus was exhausted to 1/100th of a millimetre, and observations of the pressure were made at intervals during a fortnight.

The results obtained with hydrogen may therefore be taken as being well established.

7. The argon used in these experiments was obtained from a cylinder supplied by the British Oxygen Company. The gas contained about 10 per cent. of nitrogen, which was removed by Rayleigh's method. It was admitted to a vessel containing a solution of caustic potash, and oxygen added in excess of the amount required to combine with the nitrogen. Two platinum electrodes were sealed into tubes leading into the vessel, and a discharge was passed between the electrodes for several hours. The change of pressure in the gas due to the combination of the oxygen and nitrogen was noted, and after sparking for about fifteen hours the pressure was found to remain constant. The residual traces of nitrogen were removed by continuing the sparking for several hours. The gas was then passed slowly over hot copper-foil and into a drying vessel containing phosphorus pentoxide.

Two quantities of argon were thus prepared, one having had the traces of nitrogen removed by sparking for 120 hours and the other for 70 hours. These specimens of argon will be referred to as the first and second respectively.

The velocities  $u$  and  $W$  were determined with both specimens over large ranges of electric forces and pressures. With the smaller pressures from 2 to 30 millimetres, where  $Z/p$  is large there was not much difference between the two specimens, but with the larger pressures from 30 to 150 millimetres, where the range of the ratio  $Z/p$  was from  $\cdot 1$  to  $\cdot 8$ , there was a considerable difference. With these values of the ratio  $Z/p$  the velocities of agitation were greater, and the velocities in the direction of the electric force were smaller, in the first specimen than in the second. These results indicate the presence of a small trace of impurity in the second specimen. From our previous experiments we found that the loss of energy of an electron in a collision with a molecule of argon is much less than in a collision with a molecule of nitrogen or of any other impurity that the gas might be likely to contain. Small traces of impurities have therefore the effect of reducing the velocity of agitation of the electrons, with the result that the velocities in the direction of the electric force are increased.

8. The following table gives examples of the experiments made with the first specimen of argon. The pressures  $p$  of the gas are given in millimetres of mercury, the electric force  $Z$  in volts per centimetre, and the velocity in the direction of the electric force  $W$  in cm. per sec. The quantity  $k$  is the factor by which the energy of agitation of an electron exceeds the energy of a molecule of a gas at  $15^{\circ}\text{C}$ .

The velocities  $W$  and the factors  $k$  for electrons moving in argon and in hydrogen may be compared by the curves in figs. 4, 5, and 6.

The curves (fig. 4) give the velocities  $W$  in argon and in hydrogen corresponding to the lower values of the ratio  $Z/p$  from  $\cdot 1$  to 2. The velocities corresponding to the larger values of  $Z/p$  are given in fig. 5 for argon, hydrogen, and a mixture of hydrogen and argon in the proportion by pressure of one of hydrogen to 24 of argon. In the ratio  $Z/p$  for the mixture,  $p$  is the partial pressure of the hydrogen.

The values of  $k$  are given in fig. 6. There are two curves for each gas, the lower curves I giving  $k$  for the smaller values of  $Z/p$  from  $\cdot 06$  to  $1\cdot 6$ , as indicated by the scale at the foot of the diagram, and the upper curves II for the larger

TABLE II.

$p.$	$Z.$	$Z/p.$	$k.$	$W \times 10^{-5}.$
150	16.8	0.112	96	3.12
100	10.5	0.105	95	—
100	16.8	0.168	111	3.24
150	33.6	0.224	130	—
80	16.8	0.21	126	3.3
80	33.7	0.42	170	—
50	21	0.42	172	3.64
40	33.8	0.845	273	5.85
40	50	1.25	322	—
20	42.5	2.12	340	15.2
15	42.5	2.83	320	22.6
10	42.5	4.25	312	34.0
7.2	42.5	5.9	306	46.0
4.85	42.5	8.76	324	60.4
3.5	42.5	12.1	326	72.7
2.15	42.5	19.8	324	95

Fig. 4.

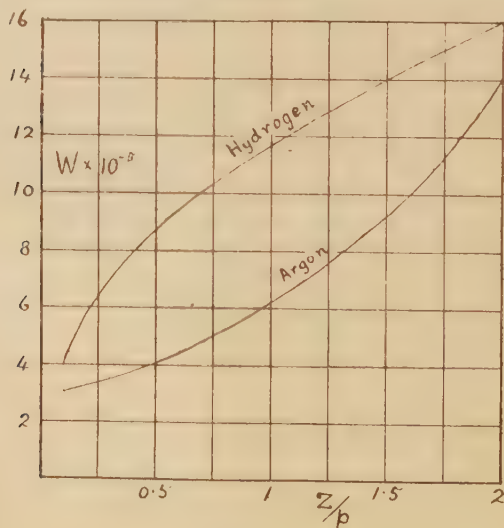


Fig. 5.

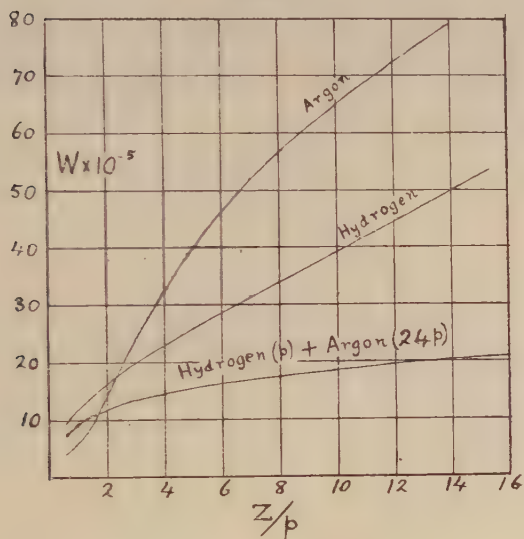
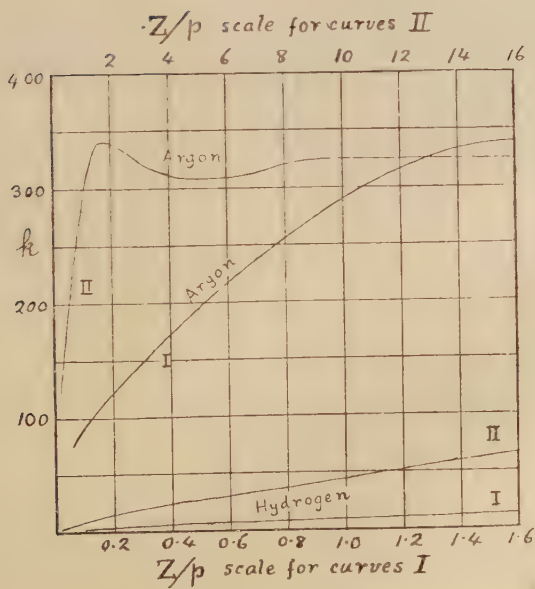


Fig. 6.



values of  $Z/p$  up to 16, as indicated by the scale at the top of the diagram. Taking  $p$  as unity, the curves for argon show that as the force increases,  $k$  increases rapidly and attains the value 340 when  $Z$  is 1.6 volts per centimetre, and after a diminution to 310 at 5 volts per centimetre,  $k$  rises again to 325 at 9 volts per centimetre and remains constant at that value for the larger forces.

9. The mean free path  $l$  of an electron may be obtained from the formula for the velocity  $W$  :

$$W = \frac{Zel}{mu} \times .815 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This formula for the velocity of the electrons is obtained from Langevin's more general formula for ions or electrons when the velocities of agitation are distributed about the mean velocity  $u$  according to Maxwell's law,  $u$  being the square root of the mean square of the velocities of agitation.

It is difficult to determine the distribution in the case of electrons moving under an electric force, and according to Pidduck's \* calculations the factor .92 is more correct than .815, but the exact value of the numerical factor is uncertain, as the mean free path depends on the velocity of the electron. The general conclusions obtained from the experiments as to the relative lengths of the free paths in different gases or the variations of the free paths with the velocity do not depend on the value attributed to the numerical factor in the formula, and as the value .815 has already been used in previous calculations, it is desirable to retain it for purposes of comparison.

The effect of a collision on the velocity of an electron may be shown by calculating the coefficient of elasticity  $f$  by Pidduck's formula. This method was adopted in the earlier researches on the motion of electrons in air †, and in those on oxygen, hydrogen, and nitrogen which were published recently ‡.

It is simpler, however, to give the proportion of the energy of an electron which is lost in a collision, as this quantity is found directly from the experimental results. The loss of energy of an electron in a collision may be estimated approximately from elementary considerations.

\* F. B. Pidduck, Proc. Lond. Math. Soc. vol. xv. pp. 87-127 (1915-16).

† J. S. Townsend and A. T. Tizard, Proc. Roy. Soc. A, lxxxviii. p. 336 (1913).

‡ Phil. Mag. Dec. 1921.



When moving along its free paths between collisions the mean velocity of an electron in the direction of the electric force is  $W$ ; and since all directions of motion are equally probable after a collision, the mean velocity in the direction of the force is zero after a collision and  $2W$  before a collision. The loss of energy in a collision is therefore  $2mW^2$ . When variations in the mean free paths and the velocities are taken into consideration, it is found that the fraction  $\lambda$  of its mean energy of agitation  $mu^2/2$  which an electron loses in a collision is given approximately by the formula

$$\lambda = 2.46 \frac{W^2}{u^2}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The following table gives the mean velocity of agitation  $u$ , and the velocity in the direction of the electric force in argon for different values of the ratio  $Z/p$  and the values of  $l$  and  $\lambda$  obtained from the above formulæ. Since  $l$  and  $\lambda$  depend directly on the energy of agitation which is proportional to  $k$ , the values of  $Z/p$  are chosen to correspond to definite values of  $k$ . The values of  $l$  are for the gas at one millimetre pressure.

TABLE III.

$k$ .	$Z/p$ .	$W \times 10^{-5}$ .	$u \times 10^{-7}$ .	$l \times 10^2$ .	$\lambda \times 10^5$ .
120	125	3.1	11.5	20	1.79
120	195	3.25	12.6	14.7	1.64
140	275	3.4	13.6	11.8	1.54
160	355	3.6	14.5	10.3	1.52
180	440	3.85	15.4	9.44	1.54
200	525	4.15	16.3	9.02	1.60
240	71	4.85	17.8	8.52	1.82
280	95	6.0	19.3	8.52	2.38
320	1.25	7.7	20.6	8.88	3.45
310	5	40	20.2	11.3	9.7
324	10	65	20.7	9.42	24.3
324	15	82	20.7	7.92	38.6

10. The large values of  $k$  obtained in argon are due to the fact that the loss of energy of an electron in a collision with a molecule is extremely small, as shown by the figures in the last column. This loss is very much less than in hydrogen or nitrogen. When moving with a velocity of agitation  $12.6 \times 10^7$  cm. per sec., the fraction of its energy lost by an electron in a collision with a molecule is  $1.6 \times 10^{-5}$  in argon,  $5 \times 10^{-2}$  in nitrogen, and  $4 \times 10^{-2}$  in hydrogen.

The increase of  $\lambda$  with the electric force when the mean velocity of agitation remains approximately constant at about  $20 \times 10^7$  cm. per sec. is clearly due to a large loss of energy in collisions with velocities greater than the mean, and a change in the distribution about the mean as  $Z$  and  $W$  increase.

As an illustration of what would take place under this condition, it may be supposed that when the velocity of an electron exceeds a value  $A$ , its velocity is reduced to  $B$  when it collides with a molecule, and while its velocity of agitation is again increased from  $B$  to  $A$ , under the action of the electric force, the electron makes several collisions with molecules in which there is very little loss of energy. The distance  $z$  that the electron travels in the direction of the electric force  $Z$  while the velocity of agitation rises from  $B$  to  $A$  is  $z = m(A^2 - B^2) / 2eZ$ , and the total number  $N$  of collisions with molecules while travelling the distance  $z$  is approximately  $uz/lW$ . Hence  $N$  is inversely proportional to the product  $ZW$ . Each collision in which there is a large loss of energy  $m(A^2 - B^2) / 2$  is therefore followed by a large number  $N$  in which the loss is negligible, so that the average loss is inversely proportional to  $N$  and therefore directly proportional to  $ZW$ . Thus, although the mean velocity of agitation remains constant, the mean loss of energy in a collision increases with  $ZW$ . In this case the velocities of agitation are distributed near the mean value  $u$  when  $Z$  and  $W$  are small, but as  $Z$  and  $W$  increase, the number of electrons with velocities near the mean diminishes and the number near the limits increases.

Another example of the effect of a change of distribution of the velocities of agitation about the mean, occurs when electrons move in pure hydrogen and in a mixture of argon and hydrogen. In hydrogen the loss of energy per collision is much greater for the larger velocities of agitation than for the smaller. Thus an effect which increases the number of electrons with velocities near the mean will reduce the average loss of energy per collision. With a constant force  $Z$  the velocity  $W$  in pure hydrogen is in many cases reduced by about 20 per cent. by adding argon to the hydrogen, while the mean velocity  $u$  of agitation remains unchanged. The loss of energy in the collisions with the argon may be neglected, so that in these cases the average loss of energy in collisions with molecules of hydrogen is proportional to  $ZW$  when the electrons are moving in pure hydrogen, and to  $ZW \times .8$  when the electrons are moving in the mixture, the reduction being due to a change in the

distribution of the velocities of agitation about the mean. In pure argon the velocity corresponding to  $k=340$  may be taken as a lower limit to the velocity at which a large loss of energy occurs in a collision. This velocity is the velocity due to a potential fall of 12.6 volts, and is a lower limit to the ionization potential.

The increase in  $\lambda \times 10^5$  from 1.54 to 1.79 in pure argon when  $u \times 10^{-7}$  changes from 13.6 to 11.5 may be due to a small quantity of impurity remaining in the gas. It will be noticed that the mean free path  $l$  changes from .118 cm. to .20 cm. with this change in  $u$ , so that the effect of an impurity would increase as  $u$  diminishes, since the proportion of the total number of collisions in which there is a considerable loss of energy increases.

11. The mean free paths of the electrons are much longer in argon than in nitrogen or hydrogen. When moving with a velocity of  $12.6 \times 10^7$  cm. per sec., the values of  $l$  are .147 cm. in argon, .029 cm. in nitrogen, and .035 cm. in hydrogen, the gases being at one millimetre pressure. If the molecules were elastic spheres of the radius  $\sigma$  which is obtained from the viscosity of argon, the mean free path of the electron in argon at a millimetre pressure would be .0286 cm.

With the range of velocities of agitation given in the table, the free path  $l$  in argon increases rapidly as the velocity diminishes, and much longer free paths would evidently be obtained if experiments were made with higher pressures and smaller forces. With the amount of pure argon at our disposal we were unable to make reliable experiments with values of  $Z/p$  less than .105, which gave  $k=95$ .

The free paths given in the tables for the velocities  $11.5 \times 10^7$  cm. per sec. and  $12.6 \times 10^7$  cm. per sec. are probably too large, as may be seen by considering the effect of a large increase of  $l$  for a comparatively small reduction in  $u$ , on the relation connecting  $W$  with  $Z$ ,  $u$ , and  $l$ . If the

formula  $W = \frac{Zel}{mu} \times 0.815$  be taken as giving accurate values

of  $l$  corresponding to the mean velocity of agitation  $u$  when a large change in  $u$  produces a small change in  $l$ , the numerical factor must be increased when a small reduction in  $u$  produces a large increase in  $l$ . The correction depends on the distribution of the velocities of agitation about the mean velocity  $u$ , and the rate of change of the mean free path with the velocity. When these two factors are taken into consideration, it is found that in the case of argon,

where the velocities  $u$  are about  $12 \times 10^7$  cm. per sec., the mean free paths obtained by the above formula may be 20 or 30 per cent. above their correct values. More accurate determinations of the mean free paths in argon for these velocities of agitation may be deduced from the mean free paths in a mixture of argon and hydrogen; and it is of interest to compare the values of  $\bar{l}$  obtained by the two methods.

12. The simplest method of finding the mean free paths in argon when the velocity of agitation is less than  $11.5 \times 10^7$  cm. per second, is to find the mean free paths in a mixture of hydrogen and argon and also in pure hydrogen, and to calculate the mean free paths in pure argon from the two sets of measurements. The velocity of agitation is controlled mainly by the hydrogen; and as there is so little loss of energy in the collisions with molecules of argon, the principal direct effect of the argon is to reduce the mean free paths of the electrons, and therefore to reduce the velocity in the direction of the electric force. In order to produce any measurable effect on the velocities of the electrons in hydrogen, it is necessary to add a large quantity of argon to it. In some previous experiments\* it was found that when the partial pressure of the argon is four times that of the hydrogen, the velocities in the mixture were not more than 10 per cent. lower than the velocities under the same forces in the hydrogen alone.

These observations show directly that the mean free path in argon for certain velocities of agitation of the electron must be of the order of fifty times the mean free paths in hydrogen at the same pressure. As no accurate conclusions could be deduced from experiments where the velocities differed by only a few per cent., the experiments were repeated, using much larger quantities of argon.

The velocities  $W$  in the direction of the electric force for a mixture containing argon at a partial pressure twenty-four times that of the hydrogen are given in fig. 5, the values of  $Z/p$  being the ratio of the electric force to the partial pressure  $p$  of the hydrogen. Thus, taking  $p=1$ , the curves show that with a force of two volts per centimetre the velocity of the electrons in pure hydrogen at a millimetre pressure is reduced from  $16 \times 10^5$  to  $11.7 \times 10^5$  cm. per second by adding argon to bring the total pressure up to 25 millimetres. The mean velocity of agitation is only reduced by 1 or 2 per cent. by the argon, so that under these conditions

\* Phil. Mag. June 1922.

the number of collisions of an electron with molecules of argon at 24 millimetres pressure is less than the number with molecules of hydrogen at one millimetre pressure.

At the higher forces the difference between the two gases is less marked.

The effect of adding 4 per cent. of hydrogen to pure argon may also be seen from the curves. Taking the case where  $Z$  is 16 and the pressure of argon 24 millimetres, the velocity  $W$  in pure argon is  $4.6 \times 10^5$  cm. per second (as shown by the point on the curve for argon corresponding to  $Z/p = .666$ ). When hydrogen at one millimetre pressure is added, the velocity is  $21 \times 10^5$  cm. per second (corresponding to  $Z/p = 16$  on the curve for the mixture). The addition of the hydrogen causes the velocity of agitation to be reduced from  $17.4 \times 10^7$  to  $8.22 \times 10^7$  cm. per second, and this change in  $u$  would not be sufficient to account for the increase in  $W$  if the mean free path in the argon were unaltered by the change in the velocity of agitation.

13. The following table gives the mean velocity of agitation  $u$ , and the velocity  $W$  in the direction of the electric force in a mixture containing 96 per cent. of argon and 4 per cent. of hydrogen by pressure, for different values of the ratio  $Z/p$ ,  $Z$  being the electric force in volts per centimetre and  $p$  the partial pressure of the hydrogen.

TABLE IV.

$k$ .	$Z/p$ .	$W \times 10^{-5}$ .	$u \times 10^{-7}$ .	$l_m \times 10^2$ .	$l_h \times 10^2$ .	$l_a \times 10^2$ .
4	.5	6.35	2.3	2.05	3.62	113
6	.75	7.95	2.82	2.09	3.39	138
8	1.0	9.1	3.26	2.08	3.06	154
10	1.28	10.0	3.64	1.99	3.88	161
13	1.72	11.1	4.15	1.87	2.66	154
16	2.25	12.2	4.6	1.75	2.49	138
20	3.25	13.6	5.15	1.51	2.29	110
30	6.55	16.7	6.3	1.12	1.99	61.5
40	10.8	19.0	7.28	.89	1.95	39.5
50	15.6	20.8	8.14	.76	2.00	29.5
70	26.0	23.5	9.62	.61	2.30	20.0
100	42.4	25.4	11.5	.48	2.98	13.6
140	64.8	26.5	13.6	.39	4.00	10.4

The mean free paths corresponding to the velocity  $u$  given in the last three columns of the table are:  $l_m$  for a mixture containing hydrogen at one millimetre pressure and argon at

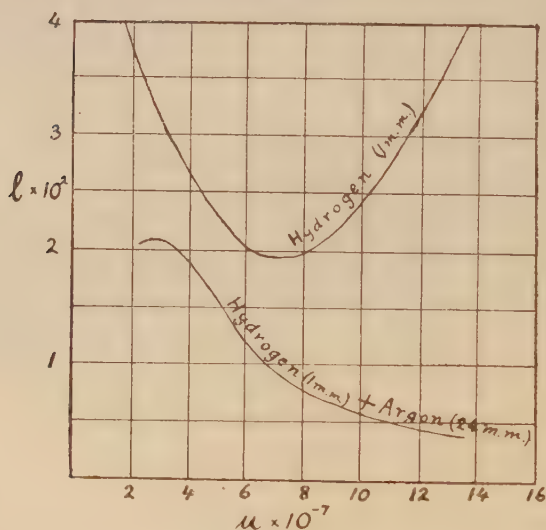


24 millimetres pressure,  $l$  for pure hydrogen at one millimetre pressure, and  $l_a$  for pure argon at one millimetre pressure. The free path  $l_a$  is obtained from  $l_m$  and  $l_h$  by means of the formula:

$$\frac{1}{l_m} = \frac{24}{l_a} + \frac{1}{l_h}. \quad \dots \dots \dots (5)$$

The free paths  $l_h$  and  $l_m$  are shown by the curves in fig. 7.

Fig. 7.



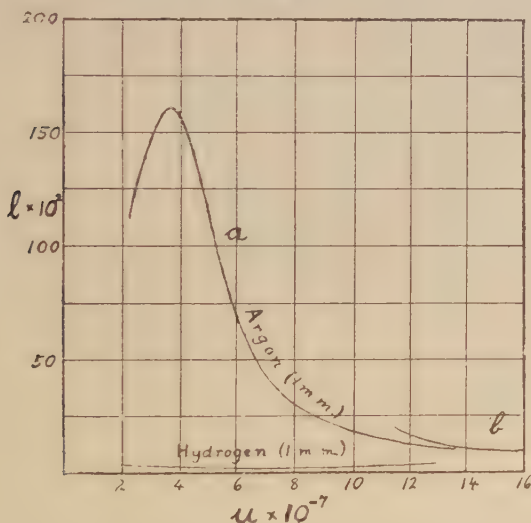
14. The free paths in pure argon at a millimetre pressure are shown by the curves (a) and (b) (fig. 8). Curve (a) for the lower velocities of agitation  $u$ , gives the free paths obtained from the measurements of velocities of electrons in a mixture of hydrogen and argon, and curve (b) the free paths obtained from the velocities in pure argon. The free paths for the range of velocities from  $11.5 \times 10^7$  to  $13.5 \times 10^7$  were found by both methods, and the curves tend to coincide with the larger velocities. Exact concordance can be expected only at points where the variation in the free path with the velocity is small, or where the velocities of agitation are very near the mean velocity  $u$ . For velocities between  $4 \times 10^7$  and  $14 \times 10^7$  there is a large increase in the free path as  $u$  diminishes; and as explained in section 11, the free path calculated by formula (4) from

measurements of  $W$  and  $u$  in pure argon is larger than the true value corresponding to the mean velocity  $u$ .

The free path of an electron in argon at a millimetre pressure has a maximum value of 1.6 cm. for the velocity  $3.75 \times 10^7$  cm. per second, which corresponds to a potential fall of .39 volt. As the value of  $l$  is an average for a number of different velocities having a mean value  $u$ , it is probable that the mean free path for electrons all moving with the velocity  $3.75 \times 10^7$  cm. per sec. is greater than 1.6 centimetres.

The free paths in hydrogen at a millimetre pressure are indicated by the lower curve in fig. 8 for purposes of comparison.

Fig. 8.



In hydrogen at a millimetre pressure the mean free path  $l$  of an electron has a minimum value of .0195 cm. when the velocity  $u$  is  $7 \times 10^7$  cm. per sec. As  $u$  diminishes  $l$  increases, and when  $u = 1.3 \times 10^7$ ,  $l = .044$ . In nitrogen a minimum value of  $l$  equal to .026 occurs when  $u = 9 \times 10^7$ , and  $l$  increases to .057 when  $u = 2.5 \times 10^7$ .

It appears from the curves showing  $l$  in terms of  $u$  that the free paths in hydrogen and nitrogen would continue to increase with further reduction in the velocity, and it is probable that in these gases  $l$  attains a maximum value

for certain velocities smaller than that corresponding to  $\cdot 2$  volt.

The large increases of the free paths of electrons as the velocity diminishes are the most remarkable of the definite results obtained from these experiments. There can be no doubt that these conclusions about the mean free paths, and the estimates of the loss of energy of the electrons in collisions with molecules, are substantially correct, notwithstanding the possible experimental errors or any uncertainty as to the exact values of the numerical coefficients in the formulæ that have been used.

XCV. *Does an Accelerated Electron necessarily radiate Energy on the Classical Theory?*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

BY the kindness of Professor Born I have learnt that the absence of radiation from the system of two oppositely charged point electrons of Lorentz mass accelerated by a uniform electric field, which I proved in a paper with this title in your March 1921 number (p. 405), also follows from a general theory which he worked out so long ago as 1909. Professor Born's paper (*Ann. d. Phys.* xxx. p. 1, 1909) forms a discussion of the theory of rigidity and of the motion of a "rigid" electron, on the basis of the principle of relativity, and one of his conclusions is given in the following words:—

"Bemerkenswerth ist, dass ein Elektron bei einer Hyperbelbewegung, so gross auch ihre Beschleunigung sein mag, keine eigentliche Strahlung veranlasst, sondern sein Feld mit sich führt, was bis jetzt nur für gleichförmig bewegte Elektronen bekannt war. Die Strahlung und der Widerstand der Strahlung treten erst bei Abweichungen von der Hyperbelbewegung auf."

This remarkable result of the early days of relativity seems to be but little known in this country, may I therefore be permitted to direct attention to it here? By "Hyperbelbewegung" is meant the motion of a particle whose world-line in the four-dimensional universe is hyperbolic, or, which comes to the same thing, the graph of which on an  $x, t$  diagram forms an hyperbola. It is the equivalent in the relativity theory of uniform acceleration in Newtonian dynamics.

Yours faithfully,  
S. R. MILNER.

September 30th, 1922.

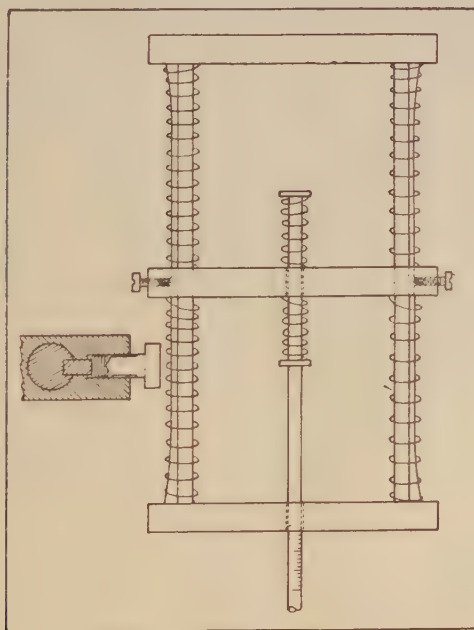
XCVI. *Simple Model to illustrate Elastic Hysteresis.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

REGARDING the very interesting paper by Mr. S. Lees, M.A., St. John's College, Cambridge, "On a Simple Model to illustrate Elastic Hysteresis" in your current issue for September, 1922, may I be permitted to refer to an earlier publication by your present correspondent in the pages of the 'Physical Review' (Ithaca, N.Y., U.S.A.) for June last.

Before the Physical Society there had been described the model illustrated below, which involved both spring and



solid frictional constraints, similar to those employed by Mr. Lees.

The model enabled the writer to explain not only mechanical hysteresis, but electrical and magnetic hysteretic systems,

involving formulæ of the type

$$B = \mu \cdot H + I.$$

The hysteresis was shown to be due, quite naturally, to the I-Component.

319 Dorset Avenue,  
Chevey Chase, Md., U.S.A.  
September 23, 1922.

I am, Gentlemen,  
Yours etc.,  
A. PRESS.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

FROM the sketch given by Mr. Press, it is quite clear that his model will produce effects analogous to those of the model described in my paper (Phil. Mag. September 1922). Until to-day, I had not seen the short abstract of Mr. Press's paper in the July (1922) number of the 'Physical Review.' I hope his full paper will be available before long.

As evidence of the curious coincidence of the papers, I note that Mr. Press's paper was read to the American Physical Society on April 21st last. My own MS. was in the hands of the publishers about April 5th last (the interval between this date and publication I am not responsible for).

Referring to my fig. 3, since the model is symmetrical about  $OO_1$ , only one-half of the model need be considered in actual practice.

I should like to emphasize a result arising out of my discussion, namely the fact that with either Mr. Press's or my own suggested model, an alteration by overstrain of the point of departure of the stress-strain curve in tension from the straight-line law, is accompanied by an alteration of the corresponding point of departure in compression. This result, although of considerable technical importance, does not appear to have received much theoretical attention.

51 Chesterton Road,  
Cambridge.  
October 6th, 1922.

Yours etc.,  
S. LEES.



XCVII. *Notices respecting New Books.*

*Cours de physique générale.* Par H. OLLIVIER. (Paris : Librairie Scientifique. J. Hermann, 1921.)

**T**HIS tome premier is devoted to a discussion of units, gravitation, electro-magnetic, in the C. G. S. system, and a new M.T.S. system (metre-tonne-second) recommended here.

What is the matter with Physics Training for Engineers? This is the question being asked to-day. The answer is sure to be: It is the C.G.S. source of Arrogance.

These niggling microscopic units are thrown aside by the young engineer as soon as he is free from the tyranny of the lecture and examination room.

They are described by Halsey in his 'Handbook for Draftsmen' as a "Monument of scientific zeal with ignorance of practical requirements. The object of Weights and Measures is to Weigh and Measure, not merely to make calculations."

The second is acclaimed as the unit of time, because it keeps *g* down to an easily remembered number for calculations. But the engineer prefers the minute to record revolutions, as an interval that can be checked with accuracy on a stop-watch. And in the astronomical units of Relativity the unit of time is nearly 1000 years.

But when it came to the choice of such diminutive units as the centimetre and gramme, in preference to the commercial metre and kilogramme, the decision was made for the supposed convenience of making the density of water unity, so that density and specific gravity would be the same number, and a name would be saved.

On the M.K.S. (metre-kilogramme system) the density of water is 1000 ( $\text{kg/m}^3$ ), with the advantage of keeping the allowance for buoyancy of the air in view, as a correction of the last figure, say a deduction of 1.25; and so a Table of Density would, if absolute, require the same deduction of 1.25 to give apparent density in air. But this correction is out of sight in the C. G. S. system, and we never hear it mentioned, although an accurate measurement must be carried out by a human being in an atmosphere where he can breathe, and not in vacuo.

The same theoretical pedantry has influenced our author in his selection of the M.T.S. system, with the same view of keeping specific gravity and density the same figure, to the same decimal, but usually ignoring the decimal when air buoyancy makes itself felt; paramount in the balloon.

A writer on Hydrostatics is equally loose when he tells us to neglect the pressure of the atmosphere. He should observe the

distinction between pressure, as gauge or absolute, as he would be compelled on changing from the non-condensing locomotive to the condensing marine engine, or in any thermodynamical calculations. In the high pressures of Internal Ballistics of Artillery, the difference may be disregarded as unimportant. But it is strange to read in an elementary text-book of this neglect, when the author is employing his favourite absolute dynamical units in Hydrostatics, and speaks of an atmospheric pressure of about seventy thousand poundals on the square foot as something of trifling account.

On the M.T.S. system with  $g=9.81$ ,  $\text{m/s}^2$  the absolute unit of force would be about the heft of 10.2 kilogrammes, and an atmosphere of one  $\text{kg/cm}^2$ , or  $10\text{t/m}^2$  would be expressed by 981 in M.K.S. units.

Our artillerist reckons his pressure in the ton  $\text{inch}^2$ , of about 150 atmospheres. A normal pressure of 20 tons  $\text{inch}^2$  would be 3000 atmospheres, or 3 million M.T.S. units; and here Halsey would begin to protest. The C.T.S. system (centimetre-tonne-second) could reduce this to 300 units, say  $3\text{t/cm}^2$  in the gravitation unit the artillerist would employ in a measurement of Force, and so on in a convenient scale for record and calculation.

It is when we come to Electro-Magnetic measurement we find the powers of 10 require such careful attention, and a system must be selected of universal acceptance in broadcasting the theory.

*A Comprehensive Treatise on Inorganic and Theoretical Chemistry.* By Dr. J. W. MELLOR. Vol I. pp. xvi+1065. Vol. II. pp. viii+894. (London: Longmans, Green & Co. 1922.) £3 3s. net each vol.

DR. MELLOR has undertaken a very heavy task in attempting to write single-handed a Comprehensive Treatise on so vast a subject as is now covered by the title 'Inorganic and Theoretical Chemistry.' The two volumes of the Treatise which have been issued furnish abundant evidence of the special qualifications which Dr. Mellor has brought to his task, and of the skill and industry with which he has marshalled the data with which the volumes are so well stored. But whilst the competence and skill of the author are beyond dispute, the magnitude of the work which he has undertaken carries with it certain obvious disadvantages. Thus, in order to cope with the difficulty of bringing even a single volume to completion, instead of spending his whole life in keeping his information and indexes up to date, the author has been obliged in certain instances to adopt rather drastic methods of treatment, by resolutely closing down some sections of the book in which new information is being gathered so quickly

that perpetual re-writing would be required in order to assimilate it completely. These sections of the book happen to include those which will be perused with the greatest interest by readers of the *Philosophical Magazine*, in which Magazine so much of this newer knowledge has been published. Thus, on page 104 an estimate of the Avogadro Constant is given which dates from 1899, although later determinations are quoted on pp. 639 and 753. Again, the whole of the sections on the Atomic Theory are based on the conceptions of 20 years ago, before the complications arising from the discovery of the radio elements and of isotopes had arisen, and before the simplifying factors introduced by the experimental determining of atomic numbers had appeared or made their influence felt. Strictly speaking, this omission applies only to the text, since the list of International Atomic Weights on page 199 and the Periodic Table on page 256 have been revised to include Atomic Numbers, as well as Atomic Weights; but these are not referred to in the index nor explained in the text, although atomic numbers are mentioned on page 255 and isotopes on page 266 as subjects for discussion in a future volume. In view of the masterly way in which he has dealt with other subjects, there can be little doubt that these later discoveries will be adequately described and discussed in the volume which deals with the radioactive elements; but there are many paragraphs, such as the one on page 200, where the inquiry is made as to whether the atomic weights are whole numbers, which would certainly have been written otherwise if the facts in reference to isotopes had been known when the text was first drafted. Again, a considerable part of the author's very able discussion of the classification of the elements is tedious to the point of positive irritation to a reader who is accustomed to see all these problems simplified, even if not completely solved, with the help of atomic numbers. The fact that certain of these sections are already out of date, if not actually incorrect, is part of the penalty which must be exacted from anyone who insists on being the author rather than the editor of a "Comprehensive Treatise" on a rapidly growing science with two thousand years of history behind it. It is necessary to add that the chapter on Crystals and Crystallization bears no evidence of being rendered obsolete or of requiring to be re-written in the light of modern work on the analysis of crystal structure by X-rays, of which a satisfactory summary is given, including references as recent as 1920. Moreover, the author's reputation, both as a mathematician and as a physical chemist, is a sufficient guarantee of the adequate treatment of subjects such as reaction velocities and energetics, where there is no risk of obsolescence arising from rapid new developments, so that the problems can be reviewed and the sections written up at leisure.

The chemical, as contrasted with the physical, portion of the work calls for nothing but admiration; and whilst the Treatise

has been based mainly on the requirements of chemists, physicists will also find it of pre-eminent value as a work of reference, to which they can turn for information on all the chemical topics which are covered by the title.

*Science in the Service of Man: Electricity.* By SYDNEY G. STARLING. (Longmans Green & Co., 1922; price 10s. 6d. net.)

THE object of this book is to give the general reader an account of the present stage of electrical knowledge.

After a brief historical sketch the industrial applications are dealt with, such as the electro-magnet, dynamo, electro-motor, telegraph, telephone and alternating current transformer.

Later chapters deal with electrolysis, discharge of electricity through a gas, X-rays, radioactivity, the electro-magnet theory and wireless telegraphy.

The treatment throughout is entirely non-mathematical. A book suitable as a school prize for a boy who delights in making things for himself, as a welcome change from the schoolmaster's favourites, Scott's Poetical Works, or Macaulay's History of England.

Some dismal X-ray photographs of surgical interest cast a gloom; otherwise much of the apparatus illustrated is simple enough for a boy to make for himself.

*La théorie Einsteinienne de la Gravitation. Essai de vulgarisation de la théorie.* Par GUSTAVE MIE. (Paris: J. Hermann, 1922.)

THIS is a translation, by J. Rossignol, from the German in the *Deutsche Rundschau*, and it is addressed in book form of 100 pages to a public not supposed to be acquainted with higher mathematics, but none the less capable of appreciating the precision and clarity of the Relativity Theory.

It will serve as an introduction to the more extended treatment of Eddington's 'Relativity,' and it is an eloquent presentation in popular language of the new ideas that arise in a discussion in general company at the present day.

*Wave-lengths in the Arc Spectra of Yttrium, Lanthanum, and Cerium and the preparation of pure rare Earth Elements.* Bureau of Standards, Government Printing Office, Washington. Scientific Papers. No. 421.

THIS paper is a continuation of the work already undertaken on the mapping of the red and infra-red spectra of the chemical elements. The results for about 35 elements have so far been published, and here the results of the study of the arc spectra of



yttrium, lanthanum, and cerium are given in detail, about 175 lines for Y, 400 for La, and 1700 for Ce. Measurements from a number of Prof. Eder's spectrograms are included in these tables. The second part of the paper describes the preparation of rare earth elements in the cerium and yttrium groups. The publication is ready for distribution, and those interested may obtain a copy by addressing a request to the Bureau until the free stock is exhausted.

*The Journal of Scientific Instruments: A monthly publication dealing with their principles, construction and use.* Produced by the Institute of Physics with the cooperation of the National Physical Laboratory. Preliminary Number. [Institute of Physics, 10 Essex St., Strand. W.C. 2.]

THIS preliminary number of a proposed Journal of Scientific Instruments is due to the recognition of the fact that there is no journal in the English language which covers the ground described in its title. Incidental descriptions of apparatus undoubtedly appear in researches published in other periodicals; but there is no room in such cases to give more than casual accounts; and moreover the accounts that are given appeal only to the few that are interested in the main subject of the paper while instruments are usually of value for researches of quite different character from those for which they were originally developed. It is intended in the proposed journal to give measured drawings of instruments as well as a scientific examination of their design.

This is a sample number and it has been distributed broadcast amongst scientific and industrial people. The possibility of this free distribution was made possible by a grant from the Treasury, through the Department of Scientific and Industrial Research.

It is not confined to any one branch of science. There is no department in which instruments are not used. The present number shows that it is intended to cater for them all. Physiology, Astronomy, Ordnance Survey, Optics, Aeronautics, Engineering, Laboratory Arts, are all represented in the present number.

The publication of a journal of this kind is a work of national importance. During the war great advances were made in many directions largely due to the scientific aid that was given to makers in the design and construction of instruments intended for novel purposes. This journal will tend to perpetuate such cooperation; and should serve as a continuous stimulus to the manufacturer.

The preliminary number can only be succeeded by others if the project receives sufficient promise of support. We are asked by The Institute of Physics to mention that a great many persons who have received a copy of the preliminary number of the proposed Journal and who may wish to support it have not yet filled



in the form inserted in the Journal. It is hoped that all who intend to subscribe will inform the Institute without delay so that an estimate may be formed of the support which may be relied upon.

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XCVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 288.]

February 17th, 1922.—Mr. R. D. Oldham, F.R.S., President,  
in the Chair.

THE President delivered his Anniversary Address, the subject of which was the Cause and Character of Earthquakes, using the word in its original sense of the disturbance which can be felt and, when severe, causes damage, as apart from that which gives rise to distant records, only obtainable by special instruments. The character is sufficiently established as a form of elastic wave-motion, of extreme complexity; this is present in all cases, and may be distinguished as the orchesis of the earthquake. In addition there is, in some cases, a molar, permanent, displacement of the solid rock, which forms the mochleusis. Further it has been shown, definitely in one case and inferentially in others, that, where mochleusis is present, the disturbance of the surface-rocks, to which the earthquake proper can be referred, is only the secondary result of a more deep-seated disturbance, which has been distinguished as the bathyseism. The origin of the elastic wave-motion must be a sudden disturbance of some sort; the depth of origin can, in many cases, be shown to be very moderate, not more than about 10 miles, and in this outer portion of the Earth's crust the only sudden disturbance conceivable is fracture, due to strain in excess of the power of resistance. In certain cases such fracture, accompanied or not by displacement, has been recognized at the surface; and measurements of the displacements show that a state of strain must have existed before actual rupture took place, but give no indication of the rate of growth of the strain. The commonly-accepted notion that the growth must be very slow appears to depend on the assumption that the strain is due to the same causes as those that have produced the folding and faulting of the surface-rocks, and also on the assumption that tectonic, as other geological processes, must necessarily be slow. The problem can only be attacked through the variation in the frequency of earthquakes; the precautions needed in applying this method are indicated, and, when applied, leave only one existing record available, the Italian one. A discussion of this shows that the rate of growth of strain is, at slowest, such that the breaking-

point will, on the average, be reached in, at most, a year, and, at the quickest, may be of such rapidity as to be analogous to a separate explosion for each earthquake. The possibility of so rapid a growth of strain being due to tectonic processes, as ordinarily understood, is considered and rejected, so that the changes by which the strain is produced must be referred to the material below the crust. Recent researches on the change of bulk, resulting from a change in the mineral aggregation of the same material, are referred to, as indicating one means by which the required effect may be brought about; and, without restricting the possibilities of other unknown processes, the results are summarized as indicating that the cause of the great majority of earthquakes is a rapid growth of strain, and that the production of this strain must be referred to changes which take place in the material underlying the outer crust of solid rock, which is directly accessible to geological observation.

March 22nd.—Prof. A. C. Seward, Sc.D., F.R.S., President,  
in the Chair.

SIR CHARLES JOHN HOLMES, Director of the National Gallery, proceeded to deliver a lecture on 'Leonardo da Vinci as a Geologist.' The Lecturer began by referring to the growth in recent years of Leonardo's reputation as a man of science. This rapid growth led recently to a reaction, and it was now not infrequently stated that Leonardo's scientific discoveries were in the nature of fortunate guess-work, and were neither proved nor accompanied by experimental research. In view of this attitude, the Lecturer felt that he could not present any statement of Leonardo's discoveries to a scientific body, such as the Geological Society, except in the form of extracts from Leonardo's own writings, which would enable them to judge for themselves whether his scientific reputation was firmly founded or not.

Reading extracts from the translations made by Mr. McCurdy and Dr. Richter, the Lecturer pointed out how Leonardo was really the first to have a large and accurate conception of the causes underlying the physical configuration of the Earth. His studies of aqueous erosion, of the formation of alluvial plains, of the process of fossilization, and of the nature of stratification, led him to a logical conviction of the immensity of geological time, and were so far in advance of the dogmatic thought of his age, that they exposed Leonardo to the charge of atheism. There can be no doubt whatever, that if he had not confided these discoveries to the almost undecipherable script of his note-books, and kept them hidden there, he would have been one of the first and most notable of the martyrs of science.

Caution thus compelled him to work in isolation, and to keep his results concealed: he had no scientific instruments, no correspondents to furnish him with observations on geological conditions elsewhere; yet his grasp of the physical history of the portions of

Italy which he had personally visited, was so sound, so firmly based on experiment and research, and so entirely in accordance with modern knowledge, that he must be considered the one great geological predecessor of Lyell.

Since publication of his discoveries was impossible, Leonardo left a record of them in his paintings, as in the background of the 'Monna Lisa,' the 'Madonna & St. Anne,' and in a less degree in our own 'Madonna of the Rocks' in the National Gallery. Here we find pictures of the primeval world as he imagined it, when seas and lakes ran up to the foot of the mountains, to be slowly displaced and silted up by the detritus which the rain carried down from the summits. From this reconstruction the pictures derive that sense of action, apart from place or time, which has fascinated generations who could not understand Leonardo's meaning as we can understand it now.

### XCIX. *Intelligence and Miscellaneous Articles.*

#### THE BUCKLING OF DEEP BEAMS.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

I WISH to thank Professor Timoshenko for his letter in the May number of the Philosophical Magazine, in which he gives references to earlier work on the above subject. I had discovered some time ago that other people had preceded me in this investigation, but I had not taken the trouble to look up their papers as my own were already published. Since reading Professor Timoshenko's letter, I have, however, examined Mr. Michell's paper in the Philosophical Magazine for September 1899, and was astonished to find how closely my own first paper (Phil. Mag., Oct. 1918) resembled his. We have solved the same problems in much the same way, and agree perfectly except on one question, the one numbered IV. in Michell's paper, and Case 5 in mine. Here I venture to say that he is wrong, for his solution makes the torque zero at the ends, which is obviously not true for the actual problem. My second paper carries the subject a little further, but, of course, it is the first step that counts, and Professor Timoshenko does not tell us whether Michell or Prandtl made the first step.

College of Technology,  
Manchester.  
May 21st, 1922.

Yours faithfully,  
JOHN PRESCOTT.



## ON DAMPED VIBRATIONS.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

The note in *Phil. Mag.* July 1922, p. 284, entitled "Note on Damped Vibrations" gives a somewhat inadequate account of a problem treated in detail by Routh, 'Dynamics of a Particle' (1898 ed.) p. 65.

As a dynamical problem, the chief point of interest seems to have been overlooked by the author of the above note, namely, the discontinuity rendered possible by the assumption of constant friction (Routh, *l. c.*).

Some further results are easily obtained in this direction; thus if the particle is placed at rest at distance  $x_0$  from the origin it will execute  $n$  semi-vibrations (about alternative centres), where  $n$  is the least integer determined by  $|x_0| - 2nF/c^2 \leq F/c^2$ ; if the particle is projected with any velocity,  $|x_0|$  may be taken to refer to the first position of rest attained.

This excludes an easily determinable portion of the series of semi-circles considered in the note.

The extended problem, including friction proportional to the velocity, is discussed by J. Andrade, *Comptes Rendus*, 5 Jan. 1920.

Artillery College, Woolwich.  
July 18, 1922.

C. E. WRIGHT.

THE MAGNETIC PROPERTIES OF THE  
HYDROGEN-PALLADIUM SYSTEM.*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

In a Paper communicated to the Royal Society (*Proc. A*, vol. 101, p. 264, 1922), I described a number of experiments on the measurement of the specific magnetic susceptibility of samples of *palladium-black* which had been charged with different amounts of hydrogen. The results showed that the susceptibility decreased rapidly with increase of hydrogen content.

My attention has just recently been directed by Mr. H. F. Biggs to a research carried out by him and described in the *Philosophical Magazine*, xxxii. p. 131 (1916). The latter experiments were made on a sample of *palladium-foil*, the susceptibility of which was found to decrease very considerably with increase of hydrogen content, my results for *palladium-black* thus agreeing with his on crystalline palladium. Mr. Biggs' work had entirely escaped my notice, the only experiments on the magnetic properties of crystalline palladium of which I was hitherto aware being those of Graham (*Jour. Chem. Soc.* vol. xxii. p. 430, 1869). Graham's deductions seemed so extraordinary, in the light of what is now known about the magnetic property of free and

combined hydrogen, that I thought it was worth while investigating palladium-black, his experiments having been conducted on crystalline palladium.

It appears that, from Mr. Biggs' and my own experiments, there is no evidence for the existence of a highly magnetic hydrogen-palladium system, as qualitatively described by Graham, nor for the existence of a magnetic "hydrogenium," whether the palladium is in the crystalline or amorphous form.

29 Amherst Road,  
Withington, Manchester,  
July 20, 1922.

I am, Gentlemen,  
Yours faithfully,  
A. E. OXLEY.

#### SHORT ELECTRIC WAVES OBTAINED BY VALVES.

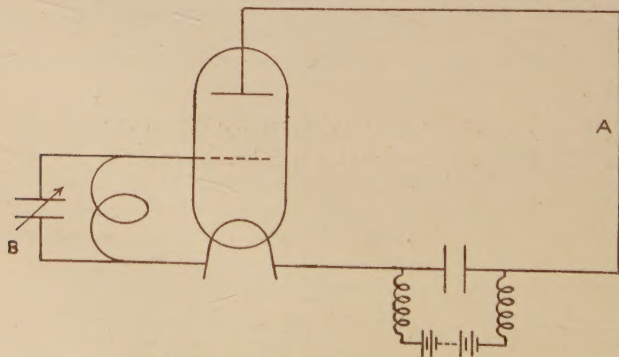
*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

In the July number of the *Philosophical Magazine* Messrs. E. W. B. Gill and J. H. Morrell have given a most interesting account of experiments with thermionic valves used to maintain electric oscillations of very high frequency.

I thought it might not be without interest to mention an alternative method of obtaining intense oscillations of short wavelength which depends for its success on the ordinary kind of electrostatic coupling in the valve.

The experiments, carried out in 1917, were never published.



The diagram illustrates the principle of the arrangement. A is a small loop of wire, which, with the capacity of the valve, forms a closed circuit of high natural frequency. B is a tunable closed circuit joining grid and filament. When B is adjusted properly vigorous oscillations occur in A which were used for the usual telegraphic and telephonic purposes.

The University, Leeds,  
July 31, 1922.

Yours faithfully,  
R. WHIDDINGTON.